High-Resolution Photoemission Study of Kondo Insulators

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Chapter 1

Introduction

1.1 Kondo insulator and Kondo metal

The appearance of Kondo effect in a Kondo-ion lattice and the formation of a heavy fermion by cooling it is one of the most profound manifestation of electron correlation in a system consisting of $f$ and conduction electrons. More striking is the temperature dependence of a dozen of nonmagnetic semiconducting rare-earth compounds such as Ce$_3$Bi$_4$Pt$_3$, CeNiSn, CeRhSb, and YbB$_{12}$ [1.1, 2]. Anomalous magnetic susceptibilities and electrical resistivities of such semiconductors, i.e., Kondo insulators, are compared with those of Kondo metals in Fig. 1.1. In Kondo insulators, the Ce or Yb ions behave as local moments above the Kondo temperature ($T_K$) and share high-temperature properties with Kondo metals. The magnetic susceptibility follows the Curie-Weiss law and the electrical resistivity is dominated by Kondo scattering resulting in the $-\log T$ behavior. In Kondo metals, as the temperature is lowered, the magnetic susceptibility reaches a constant value corresponding to an enhanced Pauli paramagnetism and the electrical resistivity decreases as $T^2$, reflecting the formation of a heavy Fermi liquid. In Kondo insulators, however, on cooling down, the magnetic susceptibility rapidly decreases after showing a broad maximum and the electrical resistivity exhibits a sharp increase in an activation form.

Reported Kondo insulators are collected in Table 1.1. A study of SmB$_6$ has a long history since its semiconducting behavior was reported in 1969 [1.3]. Note that other trivalent rare-earth hexaborides are metallic and show magnetic orders at low temperatures. Then a narrow gap in YbB$_{12}$ was reported in 1983 [1.4]. At that time, no Ce compound was reported as an intermediate-valent narrow-gap semiconductor and
Figure 1.1: Schematic representation of the magnetic susceptibility (a) and the electrical resistivity (b) of a Kondo metal (thin curves) and a Kondo insulator (thick curves).
1.1. Kondo insulator and Kondo metal

such a Table was completed only in 1990’s. Since then, the formation of narrow gaps in these compounds has been extensively studied by using various probes. Among these compounds, CeNiSn with an orthorhombic structure has been found different from the other compounds and is sometimes referred as a Kondo semimetal.

Table 1.1: Kondo insulators with their crystal structures, the activation energy ($\Delta_{\text{act}}$) determined by transport measurements, and their semiconducting analogues without 4f elements, after [1.1].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\Delta_{\text{act}}$ (K)</th>
<th>Non-f analogue</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeNiSn</td>
<td>$\varepsilon$-TiNiSn</td>
<td>3</td>
<td>TiNiSn</td>
</tr>
<tr>
<td>CeRhSb</td>
<td>$\varepsilon$-TiNiSn</td>
<td>7</td>
<td>TiNiSn</td>
</tr>
<tr>
<td>Ce$_3$Bi$_4$Pt$_3$</td>
<td>Y$_3$Sb$_4$Au$_3$</td>
<td>42</td>
<td>Th$_3$Sb$_4$Ni$_3$</td>
</tr>
<tr>
<td>Ce$_3$Sb$_4$Pt$_3$</td>
<td>Y$_3$Sb$_4$Au$_3$</td>
<td>475</td>
<td>Th$_3$Sb$_4$Ni$_3$</td>
</tr>
<tr>
<td>CeFe$<em>4$P$</em>{12}$</td>
<td>LaFe$<em>4$P$</em>{12}$</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>SmB$_6$</td>
<td>CaB$_6$</td>
<td>27</td>
<td>(SrB$_6$)$^1$</td>
</tr>
<tr>
<td>SmS</td>
<td>NaCl</td>
<td>300-3000</td>
<td>(SrS)</td>
</tr>
<tr>
<td>TmSe</td>
<td>NaCl</td>
<td>- $^2$</td>
<td>(SrS)</td>
</tr>
<tr>
<td>TmTe</td>
<td>NaCl</td>
<td>3500</td>
<td>(SrS)</td>
</tr>
<tr>
<td>YbB$_{12}$</td>
<td>UB$_{12}$</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>UFe$<em>4$P$</em>{12}$</td>
<td>LaFe$<em>4$P$</em>{12}$</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>U$_3$Sb$_4$Ni$_3$</td>
<td>Y$_3$Sb$_4$Au$_3$</td>
<td>1200</td>
<td>(Th$_3$Sb$_4$Ni$_3$)</td>
</tr>
<tr>
<td>U$_3$Sb$_4$Pd$_3$</td>
<td>Y$_3$Sb$_4$Au$_3$</td>
<td>1300</td>
<td>(Th$_3$Sb$_4$Ni$_3$)</td>
</tr>
<tr>
<td>U$_3$Sb$_4$Pt$_3$</td>
<td>Y$_3$Sb$_4$Au$_3$</td>
<td>900</td>
<td>(Th$_3$Sb$_4$Ni$_3$)</td>
</tr>
<tr>
<td>UNiSn</td>
<td>MgAgAs</td>
<td>700</td>
<td>(ThNiSn)</td>
</tr>
<tr>
<td>UPtSn</td>
<td>MgAgAs</td>
<td>2000</td>
<td>(ThNiSn)</td>
</tr>
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$^1$Parentheses indicate isostructural but not completely isoelectronic analogues.

$^2$An activation form does not fit well the electrical resistivity of TmSe.

After the observation of the semiconducting behavior of the intermediate-valent compound SmB$_6$, the hybridization gap model has been introduced for low-temperature properties of the Kondo insulator. The local moments of Kondo systems start to disappear on cooling through $T_K$ and a narrow f band is expected to be formed below
Figure 1.2: (a) Hybridized $f$ and conduction bands, leading to the hybridization gap with optical and transport gaps ($\Delta_{\text{opt}}$ and $2\Delta_{\text{act}}$), where $\Delta_{\text{opt}} > 2\Delta_{\text{act}}$. (b) Hybridization gap originated from the two bands with a similar $dE/dk$ slope. For both cases, a schematic DOS is also shown.
the coherence temperature.\textsuperscript{1} Hybridization between the narrow \textit{f} band and a broad conduction band leads to a narrow indirect gap in the case where (i) one conduction electron and one \textit{f} electron exist in the unit cell and (ii) the narrow \textit{f} band crosses only one conduction band. While a normal band insulator, which is illustrated in Fig. 1.2 (b), is expected to show an activation-type transport properties in a wide temperature range, strongly-renormalized band insulator would show such properties only below the coherence temperature, which is lower than \(T_K/3\). Here, the Coulomb repulsion \(U\) reduces both the effective band width and the gap size, but there is no qualitative change in the band structure from \(U = 0\): The band structure in Fig. 1.2 (a) is qualitatively the same as the structure in Fig. 1.2 (b) apart from the difference in the energy scale.

To discuss the Kondo insulator from the viewpoint of a renormalized band insulator, we should refer to the isostructural and isoelectronic band insulator with the \textit{f} elements replaced by elements without \textit{f} electrons. The number of valence electrons per unit cell is even for Ce-based Kondo insulators in Table 1.1, satisfying the condition of the band insulator: As shown in Table 1.1, four Ce-based Kondo insulators have their semiconducting analogues including Ti (3\textit{d}^2\textit{4s}^2) or Th (6\textit{d}^2\textit{7s}^2) at the Ce (4\textit{f}^2\textit{6s}^2) sites. The existence of such analogues without \textit{f} electrons supports the idea that the physics of Kondo insulators is qualitatively the same as the band insulator with \(U = 0\) as far as the low-temperature properties are concerned. In other words, the Kondo insulators are expected to be good semiconductors with greatly reduced gaps just as the heavy Fermion metals are good Fermi liquids.

On the other hand, when one goes to another limit of \(U \to \infty\), the \textit{f}-level occupancy is fixed to unity and the Ce or Yb atom behaves as a local Kondo ion. In that case, the system is accompanied by a spin gap, which corresponds to local singlet-triplet excitation at the Kondo ion sites. It should be remembered that a single-site Anderson model reproduces most of thermodynamic and spectroscopic properties of Ce-based Kondo metals. The single-site model predicts characteristic sharp structures in the photoemission spectra (Fig. 1.3) and the strong temperature dependence of such structures. Recent progress in energy resolution has enabled the observation of the line shape of the Kondo peak (4\textit{f}^{14} \to 4\textit{f}^{13} transition for Yb compounds) near \(E_F\) since late 1980’s \[1.5\] and it has been found out that not only the deep photoemission

\textsuperscript{1} If the local moments form a long-range magnetic order by RKKY interaction, the 4\textit{f} electrons are localized even at 0 K and do not contribute the band structure near \(E_F\).

\textsuperscript{2} The magnetic susceptibility of Ce-based Kondo systems shows a maximum around \(T_K/3\).
peaks, which would rather reflect the atomic character, but also the Kondo peak is mostly reproduced by the single-site model. However, Arko et al. reported dispersions in angle-resolved photoemission spectra of the $f$ levels in Ce and U compounds both above and below $T_K$ [1.6] and showed the importance of the effect beyond the single-site model.

![Figure 1.3: Schematic illustration of the 4f spectral DOS for mixed-valent Yb (or Ce) compounds, which is observed by photoemission (PES) and inverse photoemission spectroscopy (IPES).]

The initial motivation of our angle-integrated photoemission work was to study how the intersite effect and the single-site effect, both of which are expected to play important roles in the Kondo insulator, appear in photoemission spectra. Photoemission spectroscopy (PES) is one of the most direct probes to study electronic structures among various spectroscopies. A remarkable advantage of PES applied for rare-earth compounds, where the $f$ and conduction electrons coexist, is that one can utilize the photon-energy dependence of photoionization cross sections [1.7] to probe specific orbitals with variable photon energies. Angle-integrated PES gives the momentum-integrated spectral function, i.e., the spectral density of states (DOS), truncated by the Fermi-Dirac distribution function. Since PES probes the occupied side of the Fermi
1.1. Kondo insulator and Kondo metal

level \( (E_F) \), one can study the main part of the 4\( f \) DOS in YbB\(_{12}\), which is the only Yb-based Kondo insulator.

![Figure 1.4: LDA band structure for FeSi [1.8].](image1)

![Figure 1.5: LDA band structure of YbB\(_{12}\) near \( E_F \) [1.9].](image2)

In addition to YbB\(_{12}\), we have also studied the electronic structure of FeSi with a special attention to similarity between FeSi and YbB\(_{12}\) that weakly-dispersing bands exist on the occupied side of \( E_F \) according to the band structures calculated with the local density approximation (LDA) [1.9, 8] (Fig. 1.4 and Fig. 1.5). FeSi is a narrow-gap semiconductor at low temperatures. The magnetic susceptibility of FeSi rises gradually with increasing temperatures and then shows a Curie-Weiss like decrease. Thus not
only the narrow gap at low temperature, but also the temperature dependence of the magnetic susceptibility is reminiscent of the 4f Kondo insulator [1.1] although FeSi has no f electrons. Photoemission spectra of FeSi may therefore resemble those of YbB_{12} in some respects but may not in others. The similarities and differences between YbB_{12} and FeSi would give an important information on the physics of these compounds, including the contribution of single-site and intersite interactions.

1.2 YbB_{12} and FeSi

The semiconducting behavior of YbB_{12} was first reported by Kasaya et al. [1.4]. Its properties have often been discussed together with another rare-earth-boride semiconductor SmB_{6}, but the simplicity of the 4f-level occupancy for Yb (4f^{13} and 4f^{14}), which is the same as that for Ce (4f^{1} and 4f^{0}) considering the electron-hole symmetry, is a remarkable advantage of studying YbB_{12}. An Yb atom in YbB_{12} is almost a Kondo ion (Yb^{3+}) while a Sm atom in SmB_{6} has an intermediate-valent character (Sm^{2.6+}). RB_{12} (R = late rare-earth element) forms a NaCl-type cubic structure which consists of the rare-earth element and the B_{12} polyhedron (UB_{12} structure) as shown in Fig 1.6. In the B_{12} polyhedron, 38 electrons fill the bonding orbitals [1.10]. Since three electrons (2s^{2}, 2p^{1}) per B atom contribute to the bonding, B_{12} becomes closed-shell for the divalent anion (B_{12}^{2−}). Thus if R is a divalent cation, RB_{12} would be an insulator or a semimetal.

The magnetic susceptibility of YbB_{12} is shown in Fig. 1.7. It follows the Curie-Weiss law above \sim 170 K and Iga et al. has estimated the Yb valence to be \sim 2.85 from the Curie constant [1.12]. On cooling, it decreases rapidly after showing a broad maximum around 75 K. Since the bonding orbitals of the B_{12} polyhedron are filled by two electrons per Yb atom, nearly one electron per Yb atom is expected to contribute to the conductivity. However, the electrical resistivity of YbB_{12} rises sharply below 50 K with the activation energy of 6 meV [1.13]. Lu (4f^{14}) compounds are often good references for Yb compounds just like La (4f^{0}) compounds for Ce compounds. LuB_{12}, as well as alloy system Yb_{1−x}Lu_{x}B_{12}, has been studied as a reference of YbB_{12} [1.14]. In LuB_{12}, the Lu 4f level, which forms the closed-shell 4f^{14} configuration, is located \sim 8 eV below E_{F} [1.15].

On the other hand, the study of FeSi has a long history of more than a half century. FeSi forms a B20-type cubic structure as shown in Fig. 1.8. The B20-type structure is a modified NaCl structure, where both Fe and Si atoms are shifted along the (111)
1.2. YbB\textsubscript{12} and FeSi

Figure 1.6: (a) Crystal structure of YbB\textsubscript{12} (UB\textsubscript{12}-type structure). Yb atoms (open circles) and B\textsubscript{12} polyhedrons (shaded circles) form the rooksalt lattice [1.11]. Structure of the B\textsubscript{12} cube-octahedron after having removed the Yb atoms from YbB\textsubscript{12} and contracted the size of B\textsubscript{12} polyhedron 40 \%. The entire polyhedron is located at the center of the cell.

Figure 1.7: Magnetic susceptibility (dots) and inverse magnetic susceptibility (open circles) of YbB\textsubscript{12} polycrystals [1.13]. The line fit for the inverse magnetic susceptibility has yielded the Weiss temperature $\Theta_p = -79.1$ K.
direction. Among the 3d transition-metal monosilicides, CrSi, MnSi, FeSi, CoSi, and NiSi form the B20-type structure [1.16]. They show a variety of magnetism: MnSi shows a helical magnetic order below $\sim 30$ K, CoSi is a diamagnet, and FeSi is a narrow gap insulator which shows a gradual transition into a paramagnetic metal with increasing temperature. The semiconducting behavior of FeSi appears in the electrical resistivity and various spectroscopies (tunneling [1.17], IR [1.18, 19], photoemission [1.20–23], and Raman [1.24]). From these measurements, the activation energy of FeSi has been estimated to be 30–50 meV [1.16]. Angle-integrated PES measurements have already been performed [1.20, 21], but the interpretation of spectra has not been established. Therefore, we have studied not only the temperature dependence but also the substitution dependence of the photoemission spectra of Fe$_{1-x}$Co$_x$Si and FeSi$_{1-x}$Al$_x$ to understand the electronic structure of FeSi. We have used the He I resonance line, which mainly probes the Fe 3d orbitals [1.7], as an excitation light source. The effect of Co substitution at the Fe site and Al substitution at the Si site would appear different in photoemission spectra and response of the gap to such substitution is expected to reveal the character of the gap in FeSi.

Figure 1.8: Crystal structure of FeSi. The position coordinates are $(u, u, u)$, $(\frac{1}{2} + u, \frac{1}{2} - u, \bar{u})$, $(\bar{u}, \frac{1}{2} + u, \frac{1}{2} - u)$, and $(\frac{1}{2} - u, \bar{u}, \frac{1}{2} + u)$ with $u(\text{Fe}) = 0.1358$ and $u(\text{Si}) = 0.844$ [1.25]. The parameters $u(\text{Fe}) = 0.25$ and $u(\text{Si}) = 0.75$ give the rocksalt structure.

Figure 1.9 shows the magnetic susceptibility of FeSi. With increasing temperature, the magnetic susceptibility rises exponentially to show a broad maximum at $\sim 500$ K and then follows a Curie-Weiss law at higher temperatures. Band-structure calculation gives an almost correct gap size, but the bands at the both side of the gap
1.2. YbB$_{12}$ and FeSi

are moderately wide ($\sim$ 5 eV), while extremely ($<$ 0.1 eV) narrow bands are needed to reproduce the temperature dependence of the magnetic susceptibility [1.26]. Takahashi and Moriya [1.27, 28] reproduced the temperature dependence of the magnetic susceptibility of FeSi from a realistic wide-spread band structure by applying the spin fluctuation theory, which has been introduced by Moriya [1.29] to deal with both local and itinerant magnetism in a unified standpoint using a modified RPA scheme. Saitoh et al. measured photoemission spectra of FeSi and reproduced the low-temperature spectrum from the calculated one-electron DOS by introducing a self-energy correction to the band DOS [1.21].

Figure 1.9: Magnetic susceptibility of FeSi [1.26]. Residual paramagnetic contribution at low temperature has been subtracted. The solid curve has been calculated with a nonmagnetic ($S = 0$) ground state and a magnetic $S = 1/2$ excited state ($g = 3.92$, $\Delta = 750$ K). The magnetic susceptibility was also reproduced by a model of two narrow bands.

We compare the characteristic energy (or temperature) scales of YbB$_{12}$ and FeSi in Table 1.2. Among them, the difference in the ratio $\Delta_{\text{opt}}/(2\Delta_{\text{act}})$ between the two compounds is remarkable, where $\Delta_{\text{opt}}$ is the optical gap and $2\Delta_{\text{act}}$ is the transport
Chapter 1. Introduction

activation gap. For YbB$_{12}$ that ratio is as large as $\sim 2$ [1.30] while $\Delta_{\text{opt}}$ is just the same as $2\Delta_{\text{act}}$ for FeSi. Within the hybridization gap model, a larger difference in the dispersion slope between the two hybridizing bands would lead to a large optical gap of $\Delta_{\text{opt}} > 2\Delta_{\text{act}}$ as shown in Fig. 1.2 (a). The difference in $x_c$ reflects the importance of intersite interaction for FeSi and the localized character of the Yb 4f states.

Table 1.2: Characteristic temperature or energy scales for YbB$_{12}$ and FeSi: Peak position in the magnetic susceptibility ($T_{\text{max}}$), activation energy determined by resistivity measurements ($\Delta_{\text{act}}$), the gap in the optical conductivity ($\Delta_{\text{opt}}$), the temperature at which the gap appears in the optical conductivity ($T_{\text{gap}}$). $x_c$ is the critical substitution content at the magnetic-ion site to eliminate the semiconducting behaviors in Yb$_{1-x}$Lu$_x$B$_{12}$ and in Fe$_{1-x}$Co$_x$Si.

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{max}}$ (K)</th>
<th>$2\Delta_{\text{act}}$ (meV)</th>
<th>$\Delta_{\text{opt}}$ (meV)</th>
<th>$T_{\text{gap}}$ (K)</th>
<th>$x_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSi</td>
<td>500 [1.26]</td>
<td>60 [1.18]</td>
<td>60 [1.18]</td>
<td>200-250</td>
<td>$\sim 0.1$ [1.31]</td>
</tr>
</tbody>
</table>

To discuss the physics of FeSi connected with the 4f Kondo insulator, it should be noted that the Kondo effect appears mostly in dilute magnetic-impurity systems for transition-metal compounds$^3$. The role of Kondo effect in the paramagnetic-nonmagnetic transition is not clear in FeSi. On the contrary, such a single-site effect appears in the photoemission spectra of many Ce- and Yb-based Kondo metals.

The following Chapters are organized as follows: We describe the principles and techniques of PES in Chap. 2 and then present the results of the photoemission study of YbB$_{12}$ and FeSi in Chaps. 3-8. Chapters 3 and 4 deal with the electronic structures of YbB$_{12}$ and Yb$_{1-x}$Lu$_x$B$_{12}$ at low temperature (30 K). There we have observed both the Yb 4f and B 2sp-Yb 5d-derived conduction-band states by using various excitation energies of photons. Chapters 5 and 6 focus on the temperature dependence of the conduction-band states. We present the results of Fe$_{1-x}$Co$_x$Si in Chap. 7 and those of FeSi$_{1-x}$Al$_x$ in Chap. 8. The results of YbB$_{12}$ and FeSi are compared in the last Chapter.

$^3$ Recently, S. Kondo et al. has reported a heavy Fermi liquid behavior in LiV$_2$O$_4$ [1.32].
References


Chapter 2

Photoemission Spectroscopy

In this Chapter we present general principles and experimental technique of photoemission spectroscopy. In the section of the general principles, we express a formulation of photoemission spectrum and then show how to deduce spectral density of states (DOS) from measured photoemission spectra. In the section of the technique, we give some remarks on a pumping system for photoemission spectroscopy with a He discharge lamp and then explain a background correction for the photoemission spectra taken with a He lamp.

2.1 General Principles

2.1.1 Formulation of Photoemission Spectrum

First we present the formulation of photoemission spectrum following Gunnarsson and Schönhammer [2.1]. We assume a transition from the initial ground state $|E_0(N)\rangle$ to the final states $\psi_k^\dagger|E_n(N-1)\rangle$, where the emitted electron $|k\rangle$ has no interaction with the remaining $(N-1)$ electrons\(^1\). The golden rule gives the number of emitted electrons with the energy of $\epsilon_{out}$ as

$$P^<(\epsilon_{out}) = \sum_k \sum_n |<E_n(N-1)|\psi_k\tau|E_0(N)\rangle|^2\delta(\epsilon_{out}-\epsilon_k)\delta(\epsilon_{out}+E_n(N-1)-\hbar\nu-E_0(N))$$

(2.1)

where $\tau = \sum_{ki} \tau_{ki} \psi_k^\dagger \psi_i$ represents the transition induced by photons with a matrix element $\tau_{ki}$ between the one-electron states $|i\rangle$ and $|k\rangle$. With a further assumption of

\(^1\) This approximation becomes more accurate as the kinetic energy of the emitted electron increases.
\[ \psi_k|E_0(N)\rangle = 0, \] Eq. (2.1) is expressed as
\[ P^< (\epsilon_{\text{out}}) = \frac{1}{\pi} \sum_k \delta(\epsilon_{\text{out}} - \epsilon_k) \text{Im} < E_0(N)|\tau_k^\dagger \frac{1}{\epsilon_{\text{out}} - h\nu + H - E_0(N) - i\eta} \tau_k|E_0(N) > \] (2.2)

where \( \tau_k = \sum_i \tau_{ki} \psi_i \) and we have used the relation\(^2 \) \[ \delta(x) = \frac{1}{\pi} \text{Im} \left( \frac{1}{x - i\eta} \right). \]

Neglecting nondiagonal matrix elements corresponding to different values of \( i \), we can rewrite Eq. (2.2) as
\[ P^< (\epsilon_{\text{out}}) \propto \sum_i \frac{1}{\pi} \sum_k |\tau_{ki}|^2 \delta(\epsilon_{\text{out}} - \epsilon_k) \text{Im} G^< (\epsilon_{\text{out}} - h\nu), \] (2.3)

where
\[ G^< (z) = < E_0(N)|\psi_i^\dagger \frac{1}{z + H - E_0(N)} \psi_i|E_0(N) > . \] (2.4)

Here, we further assume that \( \sum_k |\tau_{ki}|^2 \delta(\epsilon_{\text{out}} - \epsilon_k) \) has a negligible energy dependence within the scanning region on measurement. Then Eq. (2.3) becomes proportional to \( \sum_i \text{Im} G^< (\epsilon_{\text{out}} - h\nu) \), i.e., the momentum-integrated one-particle spectral function (spectral density of states (DOS))
\[ P^< (\epsilon_{\text{out}}) \propto \sum_i \frac{1}{\pi} \text{Im} G^< (\epsilon_{\text{out}} - h\nu - i\eta) \] (2.5)
\[ = A^< (\epsilon_{\text{out}} - h\nu) \] (2.6)
\[ = \sum_{kn} |< E_n(N-1)|\psi_k|E_0(N) > |^2 \delta(\epsilon_{\text{out}} - h\nu - (E_0(N) - E_n(N-1))). \] (2.7)

Without any correlation in electrons, the remaining orbitals are frozen in the final states as they were in the initial state \(|E_n(N-1) >= \psi_k|E_0(N) > \) \[2.2\] and one can rewrite \( E_0(N) - E_n(N-1) \) as \( \epsilon_k - W \), where \( \epsilon_k \) is an energy of the orbital from which a photoelectron is emitted and \( W \) is a work function. Then the spectral DOS agrees with the DOS in the ground state as shown in Fig. 2.1:
\[ A^< (\omega) = \sum_k \frac{1}{\pi} \text{Im} \frac{1}{\omega - \epsilon_k - i\eta} = \sum_k \delta(\omega - \epsilon_k). \] (2.8)

Here we introduced the energy relative to the Fermi level \( E_F \) \( \omega = \epsilon_{\text{out}} - h\nu + W \).

By substituting \( \epsilon_k^0 + \Sigma(k, \omega) \) into \( \epsilon_k \), where \( \epsilon_k^0 \) is a bare one-electron energy and \( \Sigma(k, \omega) \) is a self energy, we can include the effect of the electron correlation as far as a quasiparticle is well defined.

\(^2\) This relation is derived straightforwardly from the representation of \( \delta \) function \( \delta(x) = \frac{1}{\pi} \frac{\eta}{x^2 + \eta^2} \).
2.1. General Principles

Figure 2.1: Principle of valence-band photoemission spectroscopy for the solids at 0 K without any correration in electrons. A photoemission spectrum reproduces the occupied part of DOS.

We can also derive the formation for the inverse photoemission spectrum and the energy distribution of the emitted photons is given as

\[ P^>(E) \propto \sum_i \frac{1}{\pi} \text{Im} G^>(E - h\nu - i\eta) \]

(2.9)

\[ = A^>(E - h\nu) \]

(2.10)

\[ = \sum_{ki} |<E_n(N+1)|\psi^\dagger_i|E_0(N)>|^2\delta(E - h\nu - (E_n(N+1) - E_0(N))) \]

(2.11)

where \( E \) is the energy of the incoming electron and

\[ G^>(\omega) = <E_0(N)|\psi_i \frac{1}{\omega - H + E_0(N)}\psi^\dagger_i|E_0(N)> . \]

(2.12)

The photoemission spectrum at finite temperature is straightforwardly given by the Lehmann representation of the temperature (Matsubara) Green function. We consider the grand canonical ensemble and use eigen states \(|\alpha'\rangle\) and \(|\alpha''\rangle\) with their eigen values \(E'\) and \(E''\) instead of \(|E_m(N)\rangle\) and \(|E_n(N-1)\rangle\).
The Fourier component of the temperature Green function is expressed as
\[
G_r (i \omega_l) = \sum_{\alpha' \alpha''} e^{\beta (\Omega - E')} \frac{e^{\beta (E' - E'')} + 1}{i \omega_l + E' - E''} < \alpha'| a_r | \alpha'' > < \alpha''| a_r^\dagger | \alpha' >
\] (2.13)
where \( \Omega \) is the thermodynamic potential.

By substituting a general complex number \( z \) for a discrete \( i \omega_l \) and exchanging \( ' \) and \( '' \), we have
\[
G_r (z) = \sum_{\alpha' \alpha''} e^{\beta (\Omega - E')} \frac{e^{\beta (E' - E'')} + 1}{z - (E' - E'')} < \alpha'| a_r | \alpha'' > < \alpha''| a_r^\dagger | \alpha' >.
\] (2.14)
and
\[
\text{Im} G_r (z) = \sum_{\alpha' \alpha''} e^{\beta (\Omega - E')} (e^{\beta (E' - E'')} + 1) < \alpha'| a_r | \alpha'' > < \alpha''| a_r | \alpha' > \delta (z - (E' - E'')).
\] (2.15)

Therefore, the imaginary part of the temperature Green function multiplied by the Fermi-Dirac (FD) function leads to the photoemission spectrum at finite temperature, which is given by averaging the initial eigenstates with the Boltzmann factors [2.1, 4]:
\[
P^<(\omega) \propto \frac{1}{\pi} \sum_{\alpha' \alpha''} e^{\beta (\Omega - E')} < \alpha'| a_r^\dagger | \alpha'' > < \alpha''| a_r | \alpha' > \delta (\omega - (E' - E''))
= (\frac{1}{e^{\beta \omega} + 1})(\frac{1}{\pi}) \text{Im} G_r (\omega)
= f(\omega) A(\omega).
\] (2.16)
where \( f(\omega) = \frac{1}{e^{\beta \omega} + 1} \) is the FD function. Similarly, the inverse-photoemission spectrum at finite temperature is given by \( P^>(\omega) \propto (1 - f(\omega)) A(\omega) \).

### 2.1.2 Derivation of Spectral DOS from Observed Photoemission Spectra

In Eqs. (2.16) we have an interest in the temperature dependence of the spectral DOS \( \text{Im} G_r (\omega) \) rather than that of FD function and we can obtain a spectral DOS of the whole energy range by dividing either photoemission spectra or inverse-photoemission spectra by each distribution factor. For simplicity, we deal with the photoemission spectra hereafter\(^3\). Experimentally observed spectra are broadened with a finite energy resolution:
\[
P_{\text{obs}} (\omega) \propto \int f(\omega_1) A(\omega_1) R(\omega - \omega_1) d\omega_1
\] (2.17)
\(^3\) We note that experimentally the energy resolution is over ten times worse for the inverse-photoemission spectroscopy than for photoemission spectroscopy.
where $R(\omega)$ is a Gaussian function. In the case for a constant spectral DOS of $A(\omega) = A$, Eq. (2.17) reduces to

$$P_{\text{obs}}(\omega) \propto A \int f(\omega_1)R(\omega - \omega_1)d\omega_1$$ \hspace{1cm} (2.18)

and division of the observed photoemission spectra by the FD function convoluted with the instrumental resolution gives the spectral DOS [2.6].

![Graph]

Figure 2.2: Top: Calculated $B_p$ partial DOS of YbB$_{12}$ (solid curve) [2.7] with the same DOS convoluted with the 7 meV Gaussian (dashed curve). Middle: Photoemission spectra for the DOS in the top panel at 6 K, 75 K, and 305 K. Bottom: Spectral DOS deduced from the spectra in the middle panel.

To show the validity of such a division for a spectral DOS with structures, we have applied that process to the calculated DOS of YbB$_{12}$ [2.7]. The top panel of Fig. 2.2

---

4 Fourier transformation for the convolution of two functions yields the product of the two functions. Shin et al. [2.5] eliminated the effect of the instrumental resolution by such transformation.
shows the $B\rho$ band DOS, both the original one and that convoluted with the Gaussian of 7 meV, which corresponds to the instrumental resolution (Chap. 5), and the middle panel shows calculated photoemission spectra, which have been obtained from the band DOS by multiplying it with FD function of each temperature and then convoluting them with the 7 meV Gaussian. We have divided these spectra by FD function of each temperature convoluted with the 7 meV Gaussian to obtain the spectral DOS as shown in the bottom panel. The obtained spectral DOS are identical below −5 meV; the 75 K and 305 K DOS perfectly reproduce the original DOS within the resolution of 7 meV. The reproducibility is not perfect for the 6 K spectrum at and above $E_F$. In the following Chapters we show such spectral DOS up to $\sim 2k_B T$ above $E_F$, where the FD function falls off to $\sim 0.1$. In the case for Fig. 2.2, the discrepancy between the deduced spectral DOS and the simply broadened DOS at $\sim 2k_B T$ is 6 %, 4 %, and 1 % for 6 K, 75 K, and 305 K, respectively.

Since we deal with the narrow-gap semiconductor of YbB$_{12}$ and FeSi, we have tried a similar simulation for a DOS with an extremely sharp structure. We show a model DOS with a square-well-shaped gap of 3 meV at $E_F$ in the top panel of Fig. 2.3 with that convoluted with the 7 meV Gaussian. The curves in the bottom panel are the DOS rederived from the calculated photoemission spectra shown in the middle panel. The derived DOS is almost identical to the simply broadened DOS even at 75 K, where the temperature width ($k_B T$) is comparable to the instrumental resolution. We have again compared the derived DOS and the original DOS and have found that the discrepancy between the deduced DOS and the simply broadened DOS up to $\sim 2k_B T$ above $E_F$ is 15 %, 8 %, and 2 % for 6 K, 75 K, and 305 K, respectively.

In the case for a spectral DOS symmetric with respect to $E_F$, one can eliminate the effect of FD function by just adding $P_{\text{obs}}(-\omega)$ to the original observed spectrum [2.8]:

$$P_{\text{obs}}(\omega) + P_{\text{obs}}(-\omega) \propto \int f(\omega_1)A(\omega_1)R(\omega - \omega_1)d\omega_1 + \int f(-\omega_1)A(-\omega_1)R(-\omega - \omega_1)d\omega_1$$

$$= \int f(\omega_1)A(\omega_1)R(\omega - \omega_1)d\omega_1 + \int (1-f(\omega_1))A(\omega_1)R(\omega - \omega_1)d\omega_1$$

$$= \int A(\omega_1)R(\omega - \omega_1)d\omega_1$$

(2.19)

where $A(-\omega) = A(\omega)$, $R(-\omega) = R(\omega)$, and $f(-\omega) = 1 - f(\omega)$.

We have applied the dividing procedure for all the temperature-dependent photoemission spectra in Chaps 5-8. In Chap. 6, the $P_{\text{obs}}(\omega) + P_{\text{obs}}(-\omega)$ procedure has also

---

5 The calculated DOS of YbB$_{12}$ is semimetallic and has a pseudogap with its bottom at 60 meV above $E_F$. 

2.2. Experimental

2.2.1 Photoemission-Spectroscopy Technique

Photoemission spectroscopy is performed in an ultrahigh vacuum chamber equipped with an excitation light source and an electron energy analyzer. An x-ray tube with Al and Mg anodes and a He discharge lamp are widely used as the photon source. We have used a VG He lamp, a Gammadata He lamp, and a synchrotron radiation ($h\nu = 125$ eV) at beam line BL-3B of the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization. For energy analysis, a
hemispherical analyzer (Fig. 2.4), where voltage is supplied to inner and outer conducting hemispheres to pass electrons with a selected energy, is adopted. We have used a VSW CLASS-150 analyzer, a Scienta SES-200 analyzer, and an Omicron EA 125 HR analyzer. These light sources and electron analyzers are commercially available now. Details are described elsewhere [2.2, 3]. We show a typical arrangement of the measurement system in Fig. 2.5. The specific measurement conditions, including temperature, pressure, surface preparation, energy calibration, and energy resolution, are described in each Chapter.

Figure 2.4: Schematic illustration of a hemispherical analyzer.

Here we make some comments on a pumping system for low-temperature photoemission spectrometers with the He lamp. We focus on the newly developed system with the VG He lamp and the Omicron EA 125 HR analyzer, which we have constructed and have improved. For photoemission spectroscopy measurements with a He lamp, a specially designed pumping system is needed. Photoelectrons excited by photons of 21.2 eV (He I α) and 40.8 eV (He II), which are emitted from the He discharge lamp, have a short escape depth of 5-20 Å [2.2] and thus an ultrahigh vacuum is required to exclude extrinsic signals owing to contaminations. However, direct connection is required between the discharge gas atmosphere of 0.1 - 10 Torr and the high-vacuum measurement chamber because no material is transparent for photons of such high energies.
Figure 2.5: Illustration of the layout of the measurement chamber [2.9], which was used in the studies of Chaps 3, 4, and 7.

The He gas that is introduced slowly into the VG lamp is differentially pumped by a rough (first) and fine (second) stage pumping and is only slightly leaked to the measurement chamber. The first and second differential stages are pumped by a rotary and a turbo pump, respectively. We have installed two turbo pumps in series as well as an ion pump to the chamber while standard ultrahigh vacuum chambers are usually closed systems with an ion pump only.\(^6\)

Typical pressures at the pumping stages and the chamber are [2.10]:

<table>
<thead>
<tr>
<th>Mode</th>
<th>First Stage</th>
<th>Second Stage</th>
<th>Chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>He I</td>
<td>5 \times 10^{-2} Torr</td>
<td>3 \times 10^{-6} Torr</td>
<td>1.5 \times 10^{-8} Torr</td>
</tr>
<tr>
<td>He II</td>
<td>5 \times 10^{-3} Torr</td>
<td>1.5 \times 10^{-7} Torr</td>
<td>5 \times 10^{-9} Torr</td>
</tr>
</tbody>
</table>

The VG lamp is designed to operate efficiently for the He I (21.2 eV) line with a relatively low intensity for the He II (40.8 eV) line. If the pressure is reduced the intensity of He II is increased and becomes comparable to the intensity of He I.

Some adsorption is critically increased at low temperatures (< 50 K) even if no

---

\(^6\) Without the turbo pump the base pressure continues to increase. He gas itself is not reactive but accumulating He gas might weaken the pumping power for other reactive gases.
contamination appears at higher temperatures under the same sample condition. Impurities through the light capillary can be an origin of the contamination. Such contamination in the photoemission spectra develops in proportion to the time of exposing the sample to the light although it does not grow while the sample is kept away from the He lamp. These impurities accompanying the He flow are difficult to detect since the local pressure at the sample position, which may be considerably different from that at the gauge tube, is responsible for contamination. Possible sources of the impurities are (i) the impurities originally included in the gas, (ii) degasing from the tube, where sufficient baking is difficult, (iii) contamination at the first stage pumping, and (iv) contamination at the second stage pumping. We discuss all of the possibilities below.

The impurities originally included in the He gas [(i)] is rather small amount. We used He gas of the highest purity (99.9999%) that is commercially available. The impurities at room temperature are:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.5 ppm</td>
</tr>
<tr>
<td>N$_2$</td>
<td>&lt; 0.1 ppm</td>
</tr>
<tr>
<td>O$_2$</td>
<td>&lt; 0.05 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>&lt; 0.02 ppm</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>&lt; 0.02 ppm</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>&lt; 0.01 ppm</td>
</tr>
</tbody>
</table>

Since the local pressure at the sample position is at least higher than that at the second stage ($3 \times 10^{-6}$ Torr), the contribution of the 1 ppm impurities, originally included in the He gas, is $3 \times 10^{-12}$ Torr at most. Nevertheless, in order to remove H$_2$O, which is the main component of the impurities in the gas, we pass the He gas into a temporary storage tank through a molecular sieve trap$^7$ cooled with liquid nitrogen.

The degasing from the tube [(ii)] might be crucial. We have installed a turbo pump for the gas-introducing tube to bake it out. Pumping only through the He lamp, whose conductance is very low, from the measurement chamber would not be sufficient on

---

$^7$ We did not provide a trap with an auto-release valve, with which a commercial molecular sieve trap is equipped, because its seal is not compatible with an ultrahigh vacuum. Thus we had to pump the trap whenever we finished passing the gas. Note that the high-pressure limit of a standard ultrahigh vacuum chamber is about 5 atm.
baking out the tube.

Entering impurities at the differentially pumping stages [(iii) and (iv)] could be the most probable origins of the contamination. In the original setup, we pumped the second stage and the rotary feedthrough of the manipulator by one turbo pump simultaneously and found that the impurities entering from the rotary feedthrough was leaked into the chamber. As for the first-stage pumping, it is equipped with a rotary pump. We have tried both a turbo pump and a rotary pump in the other system, which is equipped with the same VG lamp and the VSW CLASS-150 analyzer, and have found no impurities entering the chamber through the light capillary.

2.2.2 Background Correction

![Figure 2.6: Raw photoemission data of LuB$_{12}$, the linear background due to the satellite lines, and the background-corrected He I photoemission spectrum.](image)

Before dividing the He I (He I $\alpha$, 21.22 eV) photoemission spectrum by the FD function, one should remember that photoemission signals excited by the He II (40.8 eV) and He I $\beta$ (23.08 eV) lines, the energy of which are higher than that of He I $\alpha$, always overlap the He I spectrum as a background. Although the intensity ratio of the satellite lines to the He I $\alpha$ line is much less than one, the ratio is fixed to be
a rather high value for the Gammadata lamp (He I $\alpha$ : He I $\beta$ : He II = 82 : 8 : 10) compared with the VG lamp, of which the ratio is tunable. In the He I spectra of Yb$_{1-x}$Lu$_x$B$_{12}$, the intensity of the intrinsic signal and the background at $E_F$ are almost the same as shown in Fig. 2.6. In Chaps 5 and 7 we have subtracted a linear background before dividing the spectra by the FD function. Especially, to discuss a small change in the spectral DOS with substitution or temperature, we have subtracted the background signals systematically as follows in Chaps 6 and 8: We have assumed that the background is linear in the narrow energy region of our interest. We fitted the signals above $E_F$ in the spectra taken at 7 K to a line and subtracted that line from the raw spectra as shown in Fig. 2.6. Then we fitted the signals in the higher-temperature spectra by adjusting the intensity of the linear background at 7 K with its relative slope fixed. Although the He I spectra in Chap. 8 have been taken with the VG lamp and the satellite lines have been tuned to be much less than those with the Gammadata lamp, we have followed the above procedure to deal with the effect of a small substitution.
References


Chapter 3

Photoemission Study of YbB$_{12}$ with Variable Photon Energies

We have studied the low-energy electronic structure of a Kondo insulator YbB$_{12}$ by high-resolution photoemission spectroscopy. A "Kondo peak" is observed $\sim$25 meV below the Fermi level, which well agrees with the Kondo temperature, whereas the gap at the Fermi level is found much smaller, indicating that the magnetic properties at higher temperatures ($>\sim$75 K) are indeed determined by the Kondo effect in spite of the the gap formation at lower temperatures. A renormalized band picture is presented to describe the coexistence of the Kondo peak and the transport gap as well as the highly asymmetric lineshape of the Kondo peak.

3.1 Introduction

Correlated electron systems have fascinated researchers for decades not only because of their interesting ground-state and excited-state properties themselves but also because of their intermediate nature between the localized and itinerant limits, which often requires a new description of the phenomena or even a new physical concept. A class of $f$-electron compounds termed "Kondo insulators" have attracted considerable interest in recent years [3.1]: they are nonmagnetic insulators at low temperatures and behave as local-moment (and often metallic) systems at high temperatures. It has been controversial whether the insulating gaps are due to Kondo interaction of local character [3.2] or they are hybridization gaps renormalized by electron correlation [3.3]. In the former case, a local description of the electronic structure should be more appropriate and the
Chapter 3. Photoemission Study of YbB$_{12}$ with Variable Photon Energies

single-site Kondo temperature $T_K$ would set the energy scale of low-energy physics\[3.4\]. In the latter case, an itinerant picture or band theory, which explicitly treats the lattice periodicity, would provide a relevant starting point. It is therefore of essential importance to obtain experimental information about the low-energy electronic structure of the Kondo insulators.

In this chapter, we report on a high-resolution photoemission spectroscopy (PES) study of YbB$_{12}$, which is the only Kondo insulator among various Yb compounds \[3.6–8\]. Its magnetic susceptibility shows a Curie-Weiss behavior above $\sim 170$ K; as the temperature decreases, it shows a broad maximum at $\sim 75$ K and then rapidly decreases. The electrical resistivity and the electronic specific heat are explained by the opening of a transport gap $\Delta_c \sim 130$ K \[3.6, 7\]. Estimation of the activation energy of YbB$_{12}$ from the electrical resistivity is shown in Fig. 3.1. Among Kondo systems, Yb compounds are suitable to the study of their low-energy electronic structures by PES because within the framework of the Anderson-impurity model (AIM), a "Kondo peak" is predicted to appear below the Fermi level ($E_F$) \[3.9, 10\] and can therefore be studied with high energy resolution. Recent PES studies have indeed indicated the existence of the Kondo peak in some metallic Yb compounds \[3.11, 12\]. Our results have also revealed a Kondo peak $\sim 25$ meV below $E_F$, indicating that the same picture properly describes the Kondo insulator YbB$_{12}$ on this energy scale. The insulating behavior manifests itself on a smaller energy scale as a much smaller gap at $E_F$. In order to describe the coexistence of the Kondo peak and the tiny gap as well as the strongly asymmetric lineshape of the Kondo peak, we have employed a phenomenological renormalized $f$-band picture, starting from the band structure calculated by means of the local-density approximation (LDA) \[3.13\].

3.2 Experimental

Polycrystalline samples of YbB$_{12}$ were prepared by borothermal reduction at 2200°C and were checked to be in a single phase by x-ray diffraction. A small amount ($\sim 3\%$) of Lu was substituted for Yb to obtain good quality samples. Their magnetic susceptibility and the electrical resistivity are almost identical to those of pure YbB$_{12}$ at least for $T > 20$ K \[3.8\]. The Lu-substitution introduces $n$-type carriers into the semiconducting samples but the conductivity is rather intrinsic above $\sim 20$ K and the Fermi level is supposed to be located in the middle of the $\sim 130$ K semiconducting gap.
3.2. Experimental

Figure 3.1: Arrhenius plot for the electrical resistivity of YbB\textsubscript{12} polycrystals [3.6]. The line fit above \(\sim 15\) K gives the activation energy \(\Delta = 62\) K.

Ultraviolet PES measurements were performed with the He I and He II resonance lines (\(h\nu = 21.2\) eV and 40.8 eV, respectively) as well as synchrotron radiation at BL-3B of the Photon Factory, National Laboratory for High Energy Physics. A VSW CLASS-150 analyzer and a Scienta SES-200 analyzer were used for energy analysis. Energy calibration and estimation of the instrumental resolution were done for a Au film evaporated on the surface of the samples after each series of measurements. The resolution was 23, 42 and \(\sim 55\) meV for the He I, He II, and synchrotron radiation measurements, respectively. All measurements were done at \(30\pm5\) K. The base pressure of the spectrometer was \(\sim 7 \times 10^{-11}\) Torr for the He I and He II measurements and \(\sim 4 \times 10^{-10}\) Torr for the synchrotron radiation measurements. The surface of the samples was repeatedly scraped\textit{ in situ} with a diamond file.
3.3 Results and Discussion

Figure 3.2 shows the valence-band spectrum taken with the photon energy of 125 eV, for which the Yb 4f contribution is dominant [3.14]. The spectral features in the range from 4 eV to 13 eV are assigned to the $4f^{13} \rightarrow 4f^{12}$ multiplet structure [3.15].

![Valence-band spectrum of YbB$_{12}$](image)

Figure 3.2: Valence-band spectrum of YbB$_{12}$ in a wide energy range. For the $4f^{13} \rightarrow 4f^{12}$ part, the calculated multiplet structure [3.15] is also shown.

Between $E_F$ and 4 eV are observed $4f^{14} \rightarrow 4f^{13}$ transitions. As shown in Fig. 3.3, they consist of two sets of $4f^{13}$ spin-orbit doublets. The sharper doublet closer to $E_F$ originates from Yb atoms in the bulk and the broader one away from $E_F$ from divalent Yb atoms on the surface [3.10, 11]. The surface and bulk signals are represented by Gaussians and Mahan’s asymmetric line shapes [3.16], respectively, as shown in the figure. The Yb valence in the bulk estimated from the intensity ratio of the $4f^{13} \rightarrow 4f^{12}$

---

1 We have evaluated the intensity of the $f^{13} \rightarrow f^{12}$ signal not by integrating the signal from $-4$ to $-12$ eV but by comparing the measured line shape with an appropriately broadened $f^{13} \rightarrow f^{12}$ multiplet structure. The extra intensity can be attributed to non-negligible B 2s contribution, on the basis of the atomic photoionization cross sections of the B 2s and Yb 4f orbitals at $h\nu = 125$ eV [3.14] and the calculated B s partial density of states [3.20]. Due to the ambiguity in decomposing
3.3. Results and Discussion

Figure 3.3: $4f^{14} \rightarrow 4f^{13}$ part of the spectrum. The solid and dashed curves represent signals from the bulk and surface Yb atoms, respectively.

and $4f^{14} \rightarrow 4f^{13}$ signals is $2.86 \pm 0.06$, i.e., the number of $4f$ holes $n_f = 0.86 \pm 0.06$, in good agreement with the value $0.85$ deduced from the high-temperature magnetic susceptibility [3.17].

Figure 3.4 shows the spectra near $E_F$ taken with various photon energies. According to the photoionization cross-sections [3.14], the He I spectrum (a) is dominated by the B $2p$ contribution. In the He II spectrum (b), a weak Yb $4f$ contribution is also present as an additional intensity within $\sim 0.2$ eV of $E_F$. To extract the Yb $4f$ contribution, we have subtracted the He I spectrum from the He II spectrum and obtained a quite asymmetric peak as shown in Fig. 3.4(d). This lineshape agrees with the 125 eV spectrum (c), except for the differences due to the energy resolution and small boron contribution in the 125 eV spectrum (there is uncertainty in the region $>0.3$ eV, where the surface signals overlap). By fitting the $f$-derived spectrum using Mahan’s lineshape\textsuperscript{2} convoluted with a

the signal from $-4$ to $-12$ eV into the Yb $4f$ and B $2s$ contributions, our estimate of the intensity ratio $I(f^{13} \rightarrow f^{12})/I(f^{14} \rightarrow f^{13})$ is rather ambiguous ($= 7 \pm 3$). Nevertheless, a possible error in the evaluation of the $4f$-hole number $n_f$ by $I(f^{13} \rightarrow f^{12})/I(f^{14} \rightarrow f^{13}) = \frac{13n_f}{11(1-n_f)}$ is rather small ($n_f = 0.86 \pm 0.06$).

\textsuperscript{2} We have attempted to fit the “Kondo peak” using a symmetric Lorentzian multiplied by a Fermi-
Gaussian which represents the instrumental resolution and then removing the Gaussian convolution, we find that the peak position is \( \sim 25 \text{ meV} \) below \( E_F \), as shown by the dashed curve in Fig. 3.4 (d).

Figure 3.4: Spectra near \( E_F \) for photon energies of 21.2 eV (a), 40.8 eV (b) and 125 eV (c). (d) is the (b)-(c) difference spectrum, representing the 4f-derived spectrum. The solid curve is a fit using Mahan’s lineshape convoluted with a Gaussian representing the instrumental resolution. The dashed curve is the same curve but without the convolution.

First, we discuss the spectrum near \( E_F \) within the framework of the AIM [3.9]. In a metallic system, the Kondo temperature \( T_K \), defined as the binding energy of the Kondo Dirac function but could not reproduce the experimental spectrum for any parameter set (the position and width of the Lorentzian). If we superposed a constant background signal in order to account for the high-binding energy tail, a weak tail was extended slightly above \( E_F \) due to the finite instrumental resolution, in disagreement with experiment. Thus the high asymmetry of the peak is an intrinsic line shape that would not be affected very much by the Fermi-Dirac function.
3.3. Results and Discussion

singlet, is estimated through \( T_K \sim 3T_{\text{max}} \), where \( T_{\text{max}} \) is the temperature at which the susceptibility shows a maximum [3.19], or through \( T_K = Cn_f/\chi(0) \), where \( C = 2.57 \text{ emu K/mole} \) is the Curie constant of the Yb\(^{3+} \) ion and \( \chi(0) \) is the magnetic susceptibility at \( T = 0 \text{ K} \). In YbB\(_{12} \), since \( \chi(T) \) drops below \( T \sim 75 \text{ K} \) due to the gap formation, we have assumed that \( \chi(0) \) would take a value comparable to \( \chi(T_{\text{max}}) = 1.0 \times 10^{-2} \text{ emu/mole} \) [3.6] if the gap was not opened. Both estimations give \( T_K \sim 220 \text{ K} \). According to the AIM\(^3 \), the position of the Kondo peak \( \varepsilon_f \) measured from \( E_F \) is equal to \( k_B T_K \) in a metallic system [3.19], as has been confirmed experimentally for YbAl\(_3 \) [3.11]. In the case of YbB\(_{12} \), too, \( k_B T_K \sim 19 \text{ meV} \) is in good agreement with the experimental result of \( \varepsilon_f \sim 25 \text{ meV} \). Therefore, it seems that the Kondo effect is present both for the metallic and insulating Yb compounds in the photoemission spectra and in the magnetic susceptibility above \( T \sim T_{\text{max}} \).

The insulating nature of YbB\(_{12} \) is reflected on the He I spectrum (Fig. 3.5), which is dominated by the B \( p \) contribution. From comparison with the Fermi edge of Au in the figure, one identifies the opening of a gap or a pseudo-gap at \( E_F \)\(^5 \). In the intrinsic conduction regime, the top of the occupied valence band should be separated from \( E_F \) by the transport activation energy \( E_{\text{act}} \simeq 1/2 \Delta_c \sim 6 \text{ meV} \) [3.6]. From Fig. 3.5, one can say that the top of the valence band is at \( E_F \) or at most several meV below it, due to the limited resolution of 23 meV.

According to the band-structure calculation, YbB\(_{12} \) is a semimetal [3.20]. Since LDA underestimates band gaps [3.21], we have rigidly shifted the valence and conduction bands towards the opposite directions by hand in order to open a finite band gap and to compare the calculated density of states (DOS) with the photoemission spectra as shown in Fig. 3.5. The observed band edge is thus found to be much steeper than the calculated B \( p \) partial DOS, indicating strong renormalization (i.e., narrowing) of energy bands near \( E_F \). Since B \( sp \) states themselves are not expected to be strongly correlated, the Yb \( 4f \) components hybridizing with the B \( sp \) states should have caused the strong renormalization. A similar picture has been corroborated by an exact diagonalization

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3. The \( 4f \) orbitals show a systematic contraction as the nuclear charge \( Z \) increases in the rare earth series (lanthanide contraction) [3.18]. Thus Yb compounds are expected to be accommodated to the single-impurity description in comparison with Ce compounds.

5. AIM calculation of both magnetic susceptibility and photoemission spectra is presented in the Appendix to this Chapter.

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5. The shape of the conduction band spectrum of YbB\(_{12} \) is discussed more compared with the photoemission spectra of Yb\(_{1-x}\)Lu\(_x\)B\(_{12} \) in the following Chapters.
study of the Anderson lattice as a model for a Kondo insulator [3.22].

Therefore, we expect that the Yb 4f spectral lineshape is likewise subject to the strong renormalization of energy bands. Instead of first-principles approaches such as second-order perturbation calculations [3.23], we have employed a phenomenological approach and fitted the observed spectral lineshape using a model self-energy correction. As shown in Fig. 3.6 by the dashed curve, the Yb f partial DOS has structures from \( \sim 150 \) to \( \sim 400 \) meV while the observed peak position is \( \sim 40 \) meV below \( E_F \). This peak exhibits a steep rise from \( E_F \) as in the case of the B 2p-derived He I spectrum, and a slow tailing off on the higher binding energy side, resulting in a highly asymmetric lineshape. This indicates that the band narrowing is energy dependent and is stronger near \( E_F \). The model self-energy which we have employed to calculate the 4f spectral function \( \rho_f(\omega) \) is of the same type as that previously used for FeSi [3.13]:

\[
\Sigma(\omega) = \Sigma_h(\omega) + \Sigma_l(\omega) + \Sigma_{l'}(\omega), \tag{3.1}
\]

where

\[
\Sigma_h(\omega) = \frac{g_h(\omega - \delta)}{(\omega - \delta + i\gamma_h)^2},
\]
3.3. Results and Discussion

\[ \Sigma_j(\omega) = -g_j \left( \frac{1}{\omega - \delta + i\gamma_j} + \frac{i}{\gamma_j} \right) \quad (j = l, l'). \]

Figure 3.6: Yb 4f spectrum of YbB\(_{12}\) (dots), the Yb f partial DOS (dashed curve), the calculated spectral function \(\rho_f(\omega)\) with and without the instrumental broadening (solid curve and long dashed curves, respectively), and the quasi-particle DOS \(N^*(\omega)\) (dot-dashed curve). The self-energy \(\Sigma(\omega)\) used to calculate the spectral function is shown in the lower panel.

Here, \(-\omega\) is the binding energy measured from \(E_F\) and \(\omega = \delta \sim -5\) meV is the top of the valence band estimated from the leading-edge shift of the He I spectrum. Equation (3.1) satisfies the Kramers-Kronig (KK) relation and behaves as \(\Sigma(\omega) \sim -a(\omega - \delta) - ib(\omega - \delta)^2\) for small \(|\omega - \delta|\) as in a Fermi liquid. For simplicity, we have neglected the momentum-dependence of the self-energy [3.23, 24]. The spectrum could be best reproduced with \(g_h = 24.0\) eV\(^2\), \(\gamma_h = 4.0\) eV, \(g_l = 0.025\) eV\(^2\), \(\gamma_l = 0.08\) eV, \(g_{l'} = 0.0015\) eV\(^2\), and \(\gamma_{l'} = 0.015\) eV as shown in Fig. 3.6. The high-energy-scale component \(\Sigma_h(\omega)\) causes the shift of the structure between \(\sim0.1\) eV and \(\sim0.25\) eV in the LDA DOS to the Kondo peak (at \(\sim25\) meV below \(E_F\) after having removed the Gaussian broadening) and the shift of the structure around \(\sim0.3\) eV in the LDA DOS.
to the higher binding energy side of the peak. The low-energy-scale components, \( \Sigma_l(\omega) \) and \( \Sigma_{l'}(\omega) \) were necessary to reproduce the steep rise in the vicinity of \( E_F \). As a result, the negative slope of \( \text{Re}\Sigma(\omega) \) increases as one approaches \( E_F \). This in turn increases \( |\text{Im}\Sigma(\omega)| \) away from \( E_F \) through the KK relation, which explains how the DOS peak at \( \sim 0.3 \) eV in the LDA is smeared out and results in the asymmetric single peak in the measured spectrum. The resulting \( |\text{Im}\Sigma(\omega)| \) shows a V-shaped lineshape near \( E_F \), a reminiscent behavior of the marginal Fermi liquid proposed by Varma et al. [3.25].

In Fig. 3.6, the quasi-particle DOS \( N^*(\omega) \equiv \rho_f(\omega)(1 - \partial\text{Re}\Sigma(\omega)/\partial\omega) \) is also plotted by the dot-dashed curve.

To establish the relationship between the Kondo effect and the formation of the semiconducting gap on microscopic grounds is beyond the scope of the present phenomenological approach. In the renormalized band picture, the Kondo peak and the semiconducting gap are influenced by the different regions of the self-energy with different slopes \( \partial\text{Re}\Sigma(\omega)/\partial\omega \). However, this does not exclude the possibility that the disappearance of the local moment and that of spectral weight at \( \omega \sim 0 \) in the optical conductivity show parallel temperature dependence as in \( \text{Ce}_3\text{Bi}_4\text{Pt}_3 \) [3.2] because the electrical conductivity and the magnetic susceptibility have characteristic temperatures of similar magnitudes: \( E_{\text{act}}/k_B \sim T_{\text{max}} \). In the local description of the Kondo insulator by Kasuya [3.4], the Yb \( 4f \) hole forms a singlet bound state with a conduction electron, the binding energy being given by \( k_B T_K \). The local Kondo picture and the renormalized \( f \)-band picture should be complementary to each other, describing the different phenomena of the same correlated insulator starting from the different, i.e., localized and itinerant, limits. How the transport gap and the Kondo peak change with temperature or with electron doping (in \( \text{Yb}_{1-x}\text{Lu}_x\text{B}_12 \)) studied by PES would give further valuable information about the gap formation. Direct observation of quasi-particle dispersions using a single crystal by angle-resolved PES is also an important future subject. Finally, we remark that the strong energy dependence of mass renormalization may not be unique to the Kondo insulators but may be a general phenomenon in valence-fluctuating \( f \)-electron systems because strong asymmetry has also been reported for metallic \( \text{YbAgCu}_4 \) [3.12] and \( \text{YbAl}_3 \) [3.10].
3.4 Summary

To summarize, we have studied the low-energy electronic structure of YbB$_{12}$ using high-resolution PES. The observed position of the Kondo peak well agrees with the Kondo temperature estimated from the magnetic susceptibility above $T \sim T_{\text{max}}$, indicating that single-site Kondo effect indeed governs the magnetic properties in this temperature range in spite of the presence of the transport gap of $\Delta_c \sim 130$ K. The coexistence of the Kondo peak and the transport gap has been described in the phenomenological renormalized band picture. The mass renormalization is thus shown to be strongly energy dependent near $E_F$, leading to the highly asymmetric Kondo peak.
Appendix: Calculation of Magnetic Susceptibility

Here, we present the AIM calculation [3.26, 27] of magnetic susceptibility for the degeneracy of \( N_f = 8 \), which corresponds to the \( 4f_{7/2} \) level in Yb compounds. First we reproduced both the Kondo-peak position of \( \sim 23 \) meV and the \( 4f \)-hole occupancy of \( \sim 0.86 \) by varying the bare \( f \) \( (f^{13} \rightarrow f^{14}) \) level \( (\varepsilon_f^0) \) measured from \( E_F \) and the hybridization strength \( \Delta \) as shown in Fig. 3.7 (a). Then we calculated the magnetic susceptibility using the same parameters that were used for the calculation of the photoemission spectrum in Fig. 3.7 (a). We have found that a maximum of the magnetic susceptibility appears around \( \sim 80 \) K in Fig. 3.7 (b). Therefore, we have reproduced the peak position in the photoemission spectrum, the \( 4f \)-hole occupancy, and the maximum in the magnetic susceptibility using a single set of parameters, confirming the validity of the single-site Anderson model for YbB\(_{12}\).

![Figure 3.7: Photoemission (PES) spectrum and inverse-photoemission (BIS) spectrum (a) and magnetic susceptibility (b) calculated with the bare \( f \) level \( (\varepsilon_f^0) = 0.90 \) eV and the hybridization strength \( \Delta = \rho V^2 = 0.023 \) eV. A conduction band of 10 eV width with a constant DOS was considered and thus the magnetic susceptibility holds an enhanced Pauli paramagnetism at low temperature. Since the error increases at very low temperature, we have calculated the photoemission spectra at 10 K to deal with the Kondo-peak position.](image)
References


the Kondo peak position $\varepsilon_f$ reported for YbAgCu$_4$ may be due to the smallness of $\varepsilon_f$ compared to the instrumental resolution.


Chapter 4

Evolution of Electronic States in the Kondo Alloy System Yb$_{1-x}$Lu$_x$B$_{12}$

We have studied the effect of Lu-substitution on the Kondo insulator YbB$_{12}$ by high-resolution photoemission. Comparison of the spectra of YbB$_{12}$, Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and LuB$_{12}$ reveals that the density of states (DOS) of the B $sp$-derived conduction band near the Fermi level is reduced in YbB$_{12}$ over a rather wide ($\sim 40$ meV) energy region. Lu-substitution (i) recovers the reduced B $sp$ DOS, (ii) shifts the Yb 4$f$-derived Kondo peak towards higher binding energy and (iii) decreases the Yb valence. These results are consistently analyzed using the Anderson-impurity model, and imply interaction between the Yb 4$f$ ions mediated by the Yb 4$f$-B $sp$ hybridization in YbB$_{12}$.

4.1 Introduction

Kondo insulators have attracted many researchers’ attention due to their unique ground states and unusual low-energy excited properties [4.1–3]. In a preceding work [4.4], we have pursued this issue from the photoemission spectroscopic point of view for YbB$_{12}$, which is the only Yb-based Kondo insulator.[4.5, 6] We have found that the observed position of the Kondo peak agrees well with the Kondo temperature ($T_K$) deduced from the magnetic susceptibility in the framework of the single-impurity model. The highly asymmetric Kondo peak has been explained by a strongly energy dependent self-energy correction to the one-electron band structure [4.4, 7–9]. Since that work, some questions have remained unanswered. Firstly, there has not been a clear indication of gap opening at $E_F$ in the spectra of YbB$_{12}$ [4.10]. Secondly, the effects of hybridization between the
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Yb 4f state and B sp valence bands have not been clarified. By studying how the gap collapses with temperature, alloying and magnetic field, one may be able to answer such questions. In this Chapter, we present a photoemission spectroscopy (PES) study of the alloy system Yb$_{1-x}$Lu$_x$B$_{12}$, in which the gap closes as Lu is substituted for Yb. We have observed both the 4f- and valence-band electronic structures using various photon energies and discussed how the 4f and conduction electrons interact with each other and evolve with Lu-substitution.

Figure 4.1: Arrhenius plot for the electrical resistivity of Yb$_{1-x}$Lu$_x$B$_{12}$ [4.11].

Yb$_{1-x}$Lu$_x$B$_{12}$ has a UB$_{12}$-type crystal structure in the whole composition range 0 \( \leq x \leq 1 \). Figure 4.1 shows that the semiconducting behavior of YbB$_{12}$ persists up to \( x \sim 0.5 \) in the electrical resistivity [4.11]. The magnetic susceptibility rapidly decreases below \( \sim 60 \) K in the Yb-rich region while it saturates to a constant value in the Lu-rich region [4.11] as shown in Fig. 4.2. It shows a broad maximum at about 75 K and follows a Curie-Weiss law above \( \sim 150 \) K. Magnetic contributions to the low temperature specific heat of Yb$_{1-x}$Lu$_x$B$_{12}$ are presented in Fig. 4.3. They show a \( T \)-linear behavior in Lu-rich \( (x \geq 0.5) \) samples while in \( x \sim 0.25 \) samples they show a clear Schottky-type behavior similar to pure YbB$_{12}$ with its maximum at \( \sim 40 \) K [4.6], again
Section 4.2

4.2. Experimental

Figure 4.2: Magnetic susceptibility per mole rare earth (Yb$_{1-x}$Lu$_x$) of Yb$_{1-x}$Lu$_x$B$_{12}$ [4.11].

showing that the gap disappears only for a large amount of Lu-substitution. The Lu 4f level forms the closed-shell 4f$^{14}$ configuration and is located well below $E_F$ [4.12]. Thus in the first approximation, the extra electrons added by Lu-substitution are trapped in the Lu 4f level and do not contribute to the transport properties. Nevertheless the Lu-substitution leads to the doping of a small number of conduction electrons because the valence of Lu (3+) is somewhat larger than that of Yb (∼2.86+) [4.4].

4.2 Experimental

Polycrystalline samples of Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and LuB$_{12}$ were prepared by reducing Yb$_2$O$_3$ and Lu$_2$O$_3$ at 2200°C. The LuB$_{12}$ samples contained a trace amount (∼3%) of Yb. PES measurements were performed using He resonance lines (He I: $h\nu = 21.2$ eV and He II: 40.8 eV) and synchrotron radiation ($h\nu = 125$ eV). The latter measurements were made at beam line BL-3B of the Photon Factory, National Laboratory for High Energy Physics. The Fermi edge of Au film evaporated on the sample surface after each series of measurements was used to determine the Fermi level ($E_F$) position and the instrumental resolution. The resolution was 21-25, ∼28 and ∼55 meV for He I, He II and $h\nu = 125$ eV, respectively. All the measurements were done at ∼30 K. The base pressure of the spectrometer was ∼5 × 10$^{-11}$ Torr for the He I and He II
measurements and $\sim 3.5 \times 10^{-10}$ Torr for the synchrotron radiation measurements. The sample surfaces were repeatedly scraped \textit{in situ} with a diamond file.

### 4.3 Results and Discussion

Figure 4.4 shows the entire valence-band spectra of Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and YbB$_{12}$ (Ref. [4.4]) and their difference spectrum. For the photon energy of 125 eV used here, the Yb and Lu 4\textit{f} photoionization cross-sections are dominant [4.13]. Signals from Yb consist of two structures characteristic of valence fluctuating Yb compounds: divalent ($4f^{14} \rightarrow 4f^{13}$) and trivalent ($4f^{13} \rightarrow 4f^{12}$) parts. The divalent part is further decomposed into surface and bulk components [4.4, 14, 15] as shown in the Fig. 4.5. The bulk-surface 4\textit{f} level shift increases by about 0.1 eV in going from YbB$_{12}$ to Yb$_{0.5}$Lu$_{0.5}$B$_{12}$. For Yb$_{0.5}$Lu$_{0.5}$B$_{12}$, signals from the Lu $4f^{14} \rightarrow 4f^{13}$ transition overlap the trivalent Yb signal. Prior to subtraction, the two spectra were normalized to the trivalent Yb signal intensity so that no Yb trivalent signal appeared in the difference spectrum. In the difference spectrum, in addition to the prominent doublets from the bulk and surface Lu atoms one can see residual divalent signals of bulk and surface Yb atoms near $E_F$, indicating that the Lu-substitution causes a decrease of the Yb valence. Since the bulk residual signal amounts to $\sim 30\%$ of the bulk divalent signal in YbB$_{12}$, the Yb valence in Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ is estimated to be $\sim 2.82$ compared with Yb valence $\sim 2.86$ in YbB$_{12}$ [4.4].
4.3. Results and Discussion

$\textbf{Intensity}$

$\textbf{Yb}^{3+}$

$4f_{13}$ $\rightarrow$ $4f_{12}$

$\textbf{Yb}^{2+}$

$4f^{14} \rightarrow 4f^{13}$

$h\nu = 125$ eV

$\textbf{Yb}_{0.5}\textbf{Lu}_{0.5}\textbf{B}_{12}$

$\textbf{YbB}_{12}$

Figure 4.4: Upper panel: valence-band photoemission spectra of $\textbf{Yb}_{0.5}\textbf{Lu}_{0.5}\textbf{B}_{12}$ and $\textbf{YbB}_{12}$. Calculated multiplet structures [4.16] are also shown by vertical bars. Lower panel: the difference spectrum between $\textbf{Yb}_{0.5}\textbf{Lu}_{0.5}\textbf{B}_{12}$ and $\textbf{YbB}_{12}$.
The $h\nu = 125$ eV spectra in the upper panel of Fig. 4.6 (dots) show the Kondo peak corresponding to the $j = 7/2$ final state of the $4f^{14} \rightarrow 4f^{13}$ doublet. One notices distinct differences between the two spectra: (i) the peak for Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ is shifted toward higher binding energy by about 10 meV, and (ii) is broadened compared to that for YbB$_{12}$. In order to discuss the Yb 4$f$ signal with better resolution ($\sim 28$ meV for Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and $\sim 42$ meV [4.4] for YbB$_{12}$) we subtracted the He I spectra from the He II spectra so that the subtracted spectra, broadened with the resolution difference, agreed with the 125 eV spectra. Note that although there is Yb 4$f$ contribution in the He II spectra, the B 2$p$ contribution is dominant both in the He I and He II spectra [4.13]. For $h\nu = 125$ eV the B 2$s$ contribution, which is relatively small for He I, is not negligible [4.13] and thus we have allowed a small discrepancy between broadened He II – He I difference spectra and the 125 eV spectra on the higher binding energy side of the Kondo peak as shown in the upper panel of Fig. 4.6. As we fitted the difference spectra using Mahan’s asymmetric line shape [4.18] convoluted with a Gaussian, the Gaussian width corresponding to the instrumental resolution was sufficient to fit the
spectrum of YbB$_{12}$ while larger Gaussian broadening was needed for Yb$_{0.5}$Lu$_{0.5}$B$_{12}$. The fits show that the peak position is $\sim 23$ meV below $E_F$ for YbB$_{12}$ and $\sim 31$ meV for Yb$_{0.5}$Lu$_{0.5}$B$_{12}$.

We compare the He I spectra of YbB$_{12}$, Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and LuB$_{12}$ in the upper panel of Fig. 4.7. The figure reveals a gradual recovery of the missing spectral weight in the B 2$p$ density of states (DOS) around $E_F$ as Lu is substituted for Yb. Note that the spectral change occurs in a rather wide energy range of $\sim 40$ meV, in comparison with the transport activation energy of YbB$_{12}$ ($\sim 6$ meV). The spectrum of LuB$_{12}$ could be fitted to a linearly varying DOS multiplied by the Fermi distribution function of 30 K as shown in the lower panel of Fig. 4.7; the solid curves in the upper panel are convolutions of the DOS curves in the lower panel with the instrumental resolution. The DOS curves employed to fit the spectra of Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ and YbB$_{12}$ have a dip or pseudogap (produced by subtracting Gaussians from the linear DOS) around $E_F$. The spectral intensity at $E_F$ for YbB$_{12}$ thus turned out to be depressed by $\sim 25\%$ compared to LuB$_{12}$. Attempt to fit the spectra with a small (a few meV) but fully opened gap at $E_F$ has been unsuccessful.

The relationship between the “pseudogap” of the $\sim 40$ meV width and the $\sim 6$ meV transport gap is not clear at present. A recent electron tunneling study of SmB$_6$, which is another Kondo insulator with a transport activation energy of $\sim 4$ meV [4.19], has revealed a broad dip of $\sim 40$ meV width around $E_F$ [4.20]. Such a dip or pseudogap might be a characteristic feature of the Kondo insulators.

In the framework of the Anderson-impurity model (AIM), the properties of an Yb ion in the Kondo singlet ground state are described by [4.7]

\[ \delta = B \exp(-\frac{\pi \varepsilon_f^0}{N_f \Delta}), \quad \bar{n}_f = \frac{\Delta}{\Delta + \frac{\pi \varepsilon_f^0}{N_f}}, \]  

(4.1)

to lowest order in $1/N_f$ with $U_{ff} = \infty$, where $\delta \equiv k_B T_K$ is the Kondo peak position in the PES spectra, $B$ is the conduction-band width above $E_F$, $\varepsilon_f^0$ is the bare $f$ ($f^{13} \rightarrow f^{14}$) level measured from $E_F$ ($\varepsilon_f^0 > 0$), $N_f = 8$ is the degeneracy of the $4f_{7/2}$ level and $\bar{n}_f$ denotes the $f$-hole occupancy. We define the hybridization strength

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1 We have normalized these spectra to the intensity around $\sim 0.1$ eV to discuss only the vicinity of $E_F$. On the other hand, in Chap. 6 we normalize the He I spectra of Yb$_{1-x}$Lu$_x$B$_{12}$ single crystals to the integrated intensity between 200 meV and 260 meV. Comparison between poly- and single-crystal spectra are shown in Chap. 6.
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Figure 4.6: Photoemission spectra of Yb\(_{0.5}\)Lu\(_{0.5}\)B\(_{12}\) and YbB\(_{12}\) near \(E_F\). Upper panel: Spectra taken with \(h\nu = 125\) eV (dots) and broadened He II – He I difference spectra (solid curves). Middle panel: He II – He I difference spectra (dots) and fits using Mahan’s line shape (solid curves). Lower panel: Calculated spectra using the AIM convoluted with a Gaussian of FWHM 40 meV.
4.3. Results and Discussion

![Figure 4.7](image)

Figure 4.7: Upper panel: He I spectra of Yb\(_{1-x}\)Lu\(_x\)B\(_{12}\) and YbB\(_{12}\). The solid curves have been obtained by convoluting the curves in the lower panel with a Gaussian. Lower panel: the assumed DOS multiplied by the Fermi distribution function.

By \( \Delta = \frac{\pi}{B} \int_0^B \rho(\varepsilon) |V(\varepsilon)|^2 d\varepsilon \), where \( \rho(\varepsilon) \) is the conduction-band DOS and \( V(\varepsilon) \) is the hybridization matrix element between the \( f \) and conduction electrons [4.21]. In Yb\(_{1-x}\)Lu\(_x\)B\(_{12}\), Lu-substitution may change two parameters of the model: (i) electron doping raises the Fermi level and thus reduces \( \varepsilon_0^f \); (ii) the recovery of the B \( sp \) band DOS \( \rho(\varepsilon) \) around \( E_F \) increases \( \Delta \). With these changes in \( \varepsilon_0^f \) and \( \Delta \), \( \delta \) increases and hence \( \bar{n}_f \) decreases according to Eq.(4.1), in qualitative agreement with the PES results. However, the calculations to lowest order in \( 1/N_f \) deal with only the unoccupied side of the conduction band for Yb compounds and are not influenced by the change in the conduction-band DOS below \( E_F \) as observed in the He I spectra. Also, the line shape of the Kondo peak cannot be analyzed with lowest-order calculations, which necessarily give a single and hence symmetric peak below \( E_F \).

In order to consider the effect of changes in the B \( sp \) band near \( E_F \) on the \( f \)-electron spectra, we have calculated the 4\( f \) photoemission spectra at \( T = 0 \) K to second order in \( 1/N_f \) [4.23]. A flat DOS of 0.3 eV width is considered for the conduction band with \( E_F \).
Figure 4.8: Schematic illustration of the basis states. For Yb compounds, solid circles represent holes and open circles show electrons. The shaded parts indicate the unoccupied conduction band and the horizontal lines indicate the $f$ level [4.22].

in the middle [4.24]. We have included lowest order $f^{14}$, $f^{13}$, and $f^{12}$ states and second order $f^{14}$ state (state (0), (a), (b), and (c) in Fig. 4.8) for the calculation of the initial state [4.23] and lowest order $f^{13}$, $f^{12}$, and $f^{11}$ states and second order $f^{14}$ and $f^{13}$ states for the photoemission final states. Here, the lowest order $f^{14-n}$ state stands for the state with $n$ holes in the $f$ level and $n(n-1)$ electrons in the conduction band for the initial (final) state. An electron-hole pair is added in the second order states. Using this model, we have reproduced both the intensity ratio $I(4f^{13} \rightarrow 4f^{12})/I(4f^{14} \rightarrow 4f^{13})$, corrected for the difference in $N_f$ (= 8 and 14), and the Kondo peak position in the YbB$_{12}$ spectrum with $\Delta = 0.21$ eV, $\varepsilon_0^f = 0.7$ eV, and $U_{ff} = 7$ eV$^2$. The AIM calculations have thus given an asymmetric Kondo peak as shown in the lower panel of Fig. 4.6 although they cannot fully reproduce the experimentally observed asymmetry [4.25].

2 In our calculation, the equation $I(4f^{13} \rightarrow 4f^{12})/I(4f^{14} \rightarrow 4f^{13}) = [(N_f - 1)n_f]/[N_f(1 - n_f)]$ underestimates $\bar{n}_f$ by 5% owing to the Yb 4f-B sp hybridization. The same discrepancy has been discussed in Ref. [4.7] in the case of Ce compounds.

3 We calculated the spectra by changing the conduction-band width from 0.3 eV to 3 eV, and found that the calculated Kondo peak was most asymmetric for 0.3 eV although the total B sp band width is as large as several eV. The effectively narrow band width would be a consequence of the renormalization of those effects which do not enter the AIM explicitly. Within a single impurity model, O. Gunnarsson and K. Schönhammer [Phys. Rev. B 40, 4160 (1989)] have reported that for low-energy excitations of order $k_BT$, Coulomb interaction between the 4f and conduction electrons renormalizes the hopping
Figure 4.9: Calculated photoemission spectra which correspond to the $4f^{13} \rightarrow 4f^{12}$ transition (A) and the $4f^{14} \rightarrow 4f^{13}$ transition (B) with $U_{ff} = 7.0$ eV. We have varied $\Delta$ in (a), $\varepsilon_f^0$ in (b), and the gap width $x$ in the conduction band in (c) with other parameters fixed. All the spectra are convoluted with 40 meV Gaussian.

As already clear in Eq.(4.1), both decreasing $\Delta$ and increasing $\varepsilon_f^0$ causes qualitatively similar changes in the Kondo peak: The weight of the Kondo peak becomes smaller with its position approaching $E_F$ and the weight of the $4f^{13} \rightarrow 4f^{12}$ transition increases; the $f$-hole occupancy $\bar{n}_f$ approaches unity. As $\varepsilon_f^0$ changes, the position of the $4f^{13} \rightarrow 4f^{12}$ structure at the binding energy of about $-\varepsilon_f^0 + U_{ff}$ should be shifted by the same amount as shown in Fig. 4.9 (b). Since the shift of the $4f^{13} \rightarrow 4f^{12}$ signal is much less than 0.1 eV (Fig. 4.4), we conclude that the change of $\Delta$ rather than that of $\varepsilon_f^0$ dominates the spectral change caused by the Lu-substitution. In order to reproduce the changes in both the intensity ratio $I(4f^{13} \rightarrow 4f^{12})/I(4f^{14} \rightarrow 4f^{13})$ and the Kondo integral so that it has a maximum at $E_F$. Interaction between different Yb sites mediated by the Yb 4f-B sp hybridization might be another cause of the renormalization.
peak position in going from YbB$_{12}$ to Yb$_{0.5}$Lu$_{0.5}$B$_{12}$, $\Delta$ is varied from 0.21 eV to 0.28 eV as shown in the lower panel of Fig. 4.6 with other parameters fixed. The increase in $\Delta$ with Lu-substitution deduced from the AIM analysis is consistent with the recovery of the B $sp$ DOS near $E_F$ in the wide-energy range observed in the He I spectra. The consistent changes of the Yb 4f spectra and the B $sp$ DOS mean that the presence of the 4f-derived spectral weight near $E_F$ affects the B $sp$ DOS, which in turn affects the 4f states on neighboring Yb atoms. That is, the 4f states at different Yb sites are interacting with each other through the hybridization, indicating that the Kondo singlet in YbB$_{12}$ is not completely localized.

We have also studied the effect of gap opening in the conduction band using the AIM as presented in Fig. 4.9. We opened a narrow ($\sim 10$ meV) square-well-shaped gap locating the Fermi level at the middle of the gap, and found that the Kondo peak become narrower with its weight (and hence $\bar{n}_f$) conserved and that the high energy $4f^{13} \rightarrow 4f^{12}$ structure did not change at all. Experimentally we have indeed observed the narrowing of the Kondo peak in going from Yb$_{0.5}$Lu$_{0.5}$B$_{12}$ to YbB$_{12}$ but a substantial change in $\bar{n}_f$. Therefore the changes in the 4f spectral line shape with Lu-substitution does not necessarily imply the opening of a narrow gap in the B $sp$ DOS. The absence of the narrow gap in the PES spectra in spite of the semiconducting behavior may indicate that the states near $E_F$ are localized due to disorder or that the Fermi level is located near the bottom of the band gap.

According to the AIM, the shift of the Kondo peak with Lu-substitution should be accompanied by an increase of the Kondo temperature. Indeed the temperature where the magnetic susceptibilities reaches the maximum [4.11] increases by 10-20 K but to a lesser extent than the shift of the Kondo peak position. The maximum in the magnetic susceptibility of the insulating Yb$_{1-x}$Lu$_x$B$_{12}$ might simply have originated from missing of the Pauli paramagnetism owing to the gap opening itself. The validity of the AIM, which has only one characteristic temperature $T_K$, remains to be checked for YbB$_{12}$.

### 4.4 Summary

In summary, we have studied how Lu-substitution into YbB$_{12}$ changes the low-energy electronic structure. In going from YbB$_{12}$ to LuB$_{12}$, the broad dip in the B $sp$-derived DOS is gradually filled and the simple Fermi edge is recovered; the Kondo peak is shifted towards higher binding energy. According to the AIM analysis, the change
in the 4\textit{f} spectral line shape is caused by the recovery of the conduction-band DOS around \(E_F\). Since the recovery of the conduction-band DOS is certainly caused by the disappearance of the Yb 4\textit{f} spectral weight near \(E_F\), the present results reveal that interaction between the Yb ions is mediated by the 4\textit{f}-conduction-band hybridization and therefore that there is finite interaction between the Kondo singlets in YbB\textsubscript{12}. 
References


[4.24] The conduction band has been replaced by discrete levels $\varepsilon_k$ ($1 \leq k \leq N$) with 0.01 eV interval: see, A. Kotani, T. Jo, and J. C. Parlebas, Adv. Phys. 37, 37 (1988).
[4.25] P. Weibel, M. Grioni, D. Malterre, B. Dardel, Y. Baer, and M. J. Besnus [Z. Phys. B 91, 337 (1993)] have reported that the Kondo peak is asymmetric and broader than the single-impurity calculation for YbAgCu$_4$. 
Chapter 5

Temperature Dependence of the High-Resolution Photoemission Spectra of the Kondo Insulator YbB$_{12}$

We have performed a detailed temperature-dependent photoemission study of the conduction-band states in the Kondo insulator YbB$_{12}$ using single crystalline samples. Measurements with improved energy resolution have revealed (pseudo)gaps of two energy scales. The size of the narrower gap $\sim 10$ meV and its disappearance at high temperatures are consistent with the temperature dependence of the electrical resistivity and the magnetic susceptibility. The larger pseudogap of $\sim 100$ meV depends on temperature even at room temperature. We discuss how the characteristics of the Kondo insulator are reflected in the conduction-band photoemission spectra.

5.1 Introduction

The formation of a nonmagnetic insulating ground state in the Kondo insulator from a higher-temperature metallic state, where itinerant electrons are scattered by local moments, is one of the most intriguing phenomena in strongly correlated systems [5.1]. Among them YbB$_{12}$ is the only Yb-based Kondo insulator [5.2]. In Yb compounds, because a large part of the 4$f$ density of states (DOS) is on the occupied side of the Fermi level ($E_F$) in contrast to Ce compounds, one can study the main part of
the $f$ states by photoemission spectroscopy (PES). Actually the peculiar temperature
dependence of the $4f$ emission in Yb compounds has been studied extensively with
high-resolution PES [5.3]. However, few PES studies have so far focused on the non-$f$
conduction-band states. Schlesinger et al. remarked on the optical spectra of a “3$d$
Kondo insulator” FeSi [5.4] that the entire conduction band, which screens all the local
moments, could depend on the temperature. Such a temperature dependence could
appear in the formation of the Kondo singlet irrespective of whether the system becomes
a renormalized metal or insulator. The electrical resistivity of the Kondo insulator
is expected to be dominated by the Kondo effect at high temperatures and to show
activated behavior at low temperatures. Thus a significant temperature dependence
is expected in the conduction-band states and such a temperature dependence may
give a clue to understand the Kondo insulators. In the preceding work using $\text{YbB}_{12}$
polycrystals, we have studied the low-temperature electronic structure [5.5] and its
Lu-substitution effects [5.6] by PES. For the conduction-band states of $\text{B}_{2sp}$ - $\text{Yb}
5d$
hybridized character, we have found that a broad dip or a pseudogap of $\sim 40 \text{ meV}$
width is present and is filled gradually with Lu substitution. $\text{YbB}_{12}$ has a cubic $\text{UB}_{12}$-type
structure [5.7] and is believed to develop a rather isotropic gap at low temperatures.
In this work, we have made a PES study of $\text{YbB}_{12}$ single crystals with higher energy
resolution to investigate how the (pseudo)gap evolves as a function of temperature.

5.2 Experimental

Single crystalline $\text{YbB}_{12}$ samples were prepared using the traveling-solvent floating-zone
method [5.8]. $\text{YbB}_{12}$ forms by a peritectic reaction at $2200^\circ \text{C}$, which temperature is close
to the peritectic temperature of the adjacent phase $\text{YbB}_{66}$ ($2150^\circ \text{C}$)[5.9]. In order to
keep the temperature inhomogeneity less than $50^\circ \text{C}$ at $2200^\circ \text{C}$ we used an image furnace
with four xenon lamps. Laue photographs and x-ray powder diffraction confirmed large
samples to be single crystalline. Figure 5.1 shows the electrical resistivity and the
magnetic susceptibility of the best rod grown in this way [5.8]. The resistivity increases
monotonously by more than five orders of magnitude as the temperature is decreased
from $300 \text{ K}$ to $1.3 \text{ K}$. The activation energy ($\Delta_{\text{act}}$) for $15 \text{ K} < T < 40 \text{ K}$ is $68 \text{ K}$. The inset
shows the high-temperature ($> 100 \text{ K}$) resistivity, which follows $- \log T$. The magnetic
susceptibility is characteristic of the Kondo insulator: It follows a Curie-Weiss law above
$\sim 170 \text{ K}$ and as the temperature decreases it shows a broad maximum at $T_{\text{max}} \sim 75 \text{ K}$
and then rapidly decreases. The low-temperature upturn of the magnetic susceptibility is very small compared with that of polycrystals, indicating a much reduced amount of magnetic impurities.

Figure 5.1: Electrical resistivity and magnetic susceptibility of the YbB$_{12}$ single crystal used in the present work [5.10]. High-temperature ($100 < T < 300$ K) resistivity is plotted in the inset.

All the photoemission measurements were performed for samples cut from the rod whose magnetic and electrical properties are profiled in Fig. 5.1. We used a He I resonance line ($h\nu = 21.2$ eV) from a Gammadata He discharge lamp and a synchrotron radiation ($h\nu = 125$ eV) for excitation light sources. Scienta SES-200 analyzers were
used for energy analysis. The He I measurements were done at Hiroshima University and the synchrotron radiation measurements were done at beam line BL-3B of the Photon Factory, High Energy Accelerator Research Organization. The base pressure of the spectrometer was $\sim 1.4 \times 10^{-10}$ Torr for the He I measurements and $\sim 3.5 \times 10^{-10}$ Torr for the synchrotron radiation measurements. Liquid-He flow cryostats were used to rapidly cool the samples. The sample surfaces were scraped in situ with a diamond file and therefore the measured spectra represent the angle-integrated spectral functions, namely, the spectral densities of states. We evaporated Au on the samples after every measurement to determine the Fermi-level ($E_F$) position and the energy resolution. The resolution was 7 meV for $h\nu = 21.2$ eV and $\sim 0.14$ eV for $h\nu = 125$ eV. The data acquisition system of the He I measurements was very stable for many hours and the accuracy of $E_F$, including its fluctuation with time, was less than $\sim 0.1$ meV.

5.3 Results and Discussion

Figure 5.2 shows the entire valence band of single crystalline YbB$_{12}$ taken with the photon energy of $h\nu = 125$ eV. The Yb 4f contribution is relatively large for $h\nu = 125$ eV [5.11]. The measurement temperature was $\sim 20$ K, low enough compared with $T_{max} \sim 75$ K, where the magnetic susceptibility shows a broad maximum. The spectrum consists of two sets of structures characteristic of intermediate-valence Yb compounds, namely, the divalent ($4f^{14} \rightarrow 4f^{13}$) and trivalent ($4f^{13} \rightarrow 4f^{12}$) parts [5.12–14]. The divalent part is further decomposed into surface and bulk signals as shown in the figure. The present spectra are almost identical to those of polycrystals reported earlier [5.5] except (a) that a broad non-f contribution around $\sim 8$ eV is reduced [5.15] and (b) that the surface signal increases (probably due to the difference in the irregularity of the scraped surfaces) for the single crystal. The decrease in the non-f contribution would correspond to the improved sample quality. A possible origin of the non-f emission around $\sim 8$ eV for the polycrystals, which does not depend much on exposing time, may be impurities in grain boundaries.

Figure 5.4 shows high-resolution temperature-dependent PES spectra taken with the He I resonance line. According to the photoionization cross-sections, He I probes the B 2sp - Yb 5d-derived DOS[5.11]. We have made a series of temperature-dependent measurements without intermediate scraping: First we scraped the sample at 305 K and took spectra at that temperature. Then we measured spectra while lowering the
Figure 5.2: Valence-band photoemission spectrum of single crystalline YbB$_{12}$ ($h\nu = 125$ eV). Vertical bars for the trivalent part are multiplet structures calculated by Gerken[5.26].

temperature from 225 K to 6 K without rescraping it. All the spectra were taken in less than two hours after scraping. The spectrum taken at 6 K in this way was identical to that taken just after scraping. Several series of such measurement cycles were made and the spectra were all reproducible. The upper panel of Fig. 5.4 shows the accumulation of five series of such temperature-dependent measurements. The spectra have been normalized to the intensity below $-0.2$ eV. The two thick curves are the spectra taken at 305 K and 6 K. With increasing temperature, significant spectral weight is distributed above $E_F$ in spite of small changes below $E_F$ although in a simple metal an increase in the spectral weight above $E_F$ should compensate with a decrease below $E_F$.

In order to isolate the temperature dependence of the spectral DOS, including the phonon effect, from that of the Fermi-Dirac (FD) distribution function, we have divided
the spectra by the FD distribution function (convoluted with a Gaussian corresponding to the instrumental resolution) [5.16–18] as shown in the lower panel of Fig. 5.4. We present the spectral DOS up to $\sim 2k_BT$ above $E_F$ where the FD function falls off to $\sim 0.1$. The results show that the DOS with a V-shaped dip varies with temperature in such a wide energy region as $\sim 100$ meV around $E_F$. This widely extended dip compared with the activation energy of 6 meV has already been implied in the previous measurements on polycrystalline YbB$_{12}$ [5.5]. Here, the improved energy resolution has clarified the shape of the dip at low temperatures: The closer to $E_F$ one goes, the steeper the slope appears. From the measurements on polycrystals at $\sim 30$ K we estimated that the spectral DOS at $E_F$ was depressed by $\sim 25\%$ compared with that of LuB$_{12}$. Here, the depression amounts to more than 40\% in going from 305 K to 6 K because of the improved energy resolution and the extended temperature range. The width of the sharp cusp-like depression in the very vicinity of $E_F$, which has not been observed in the previous work, is $\sim 10$ meV. This energy scale falls in the same range as the transport gap of $2\Delta_{act} \sim 12$ meV. The appearance of this sharp depression only at low temperatures (6 to 75 K) is parallel to the temperature dependence of the magnetic susceptibility and the electrical resistivity: Below $T_{\text{max}} \sim 75$ K the magnetic susceptibility decreases due to the missing Pauli paramagnetism. The electrical resistivity follows an activated form only below $\sim 50$ K. Above $\sim 100$ K it decreases slowly with temperature following $-\log T$, like a metallic Kondo material[5.19]. Except for the residual DOS at $E_F$ at low temperatures the spectra imply that a narrow gap is formed at low temperatures while a Fermi edge exists at high temperatures. Here, we note that the bottom of the pseudogap in YbB$_{12}$ is not located exactly at $E_F$ but slightly below $E_F$. This may indicate that the dip feature are caused by hybridization of the conduction-band states with the 4$f$ states since the 4$f$ states are located largely below $E_F$.

A recent reflectivity study by Okamura et al.[5.20] has also revealed two energy scales in the spectrum of YbB$_{12}$ as shown in Fig. 5.3: a gap of $\sim 25$ meV (threshold) with a shoulder at $\sim 40$ meV develops below 70 K in the optical conductivity (Fig. 5.3 (b)). They are superposed on a broad dip with a shoulder at $\sim 0.25$ eV, which is present at all temperatures (Fig. 5.3 (b)). Okamura et al. have attributed the broad structure to a 4$f$-5$d$ transition, which has no direct relation with the peculiar behavior of the Kondo insulator. That the energy of the optical threshold is larger than the transport gap ($2\Delta_{act} \sim 12$ meV) is characteristic of an indirect gap, implying a formation of a
5.3. Results and Discussion

Figure 5.3: (a) Reflectivity ($R$) and optical conductivity ($\sigma$) of YbB$_{12}$ at 290 K (dotted-dashed curve), 160 K (dots), 78 K (dashed curve), and 20 K (solid curve). (b) $R$ and $\sigma$ in lower-energy region at 78, 70, 60, 50, 40, and 20 K from top to bottom. The inset shows the magnetic susceptibility of YbB$_{12}$ single crystal [5.20].

renormalized hybridization gap$^1$. This is contrasted with the behavior of FeSi, in which the valence-band edge is located $\sim 35$ meV below $E_F$ [5.21], nearly half of the optical gap (threshold) of $\sim 60$ meV[5.4]. The origin of the residual DOS at $E_F$ in FeSi as well as in YbB$_{12}$ remains unclear at present. This may be due to an extrinsic signal from a possibly metallic surface layer. Also, the residual DOS may have been caused partly by the finite energy resolution.

The high-temperature spectra of the conduction band is also worth remarking. The spectral DOS continues to be recovered even above 150 K and the broad V-shaped dip still survives at 305 K. The lower panel of Fig. 5.4 shows that the DOS is not conserved within $\sim 100$ meV of $E_F$, indicating spectral weight transfer with temperature over an energy scale larger than $\sim 100$ meV. Such a temperature dependence is most likely associated with changes in the 4$f$ electronic states because the presence of the Yb 4$f$

$^1$ If the narrow 4$f$ band and the broad conduction band are hybridized with each other, then the bottom of the conduction band can be far from the top of the valence band because the magnitude of the dispersion ($dE/dk$) between the two hybridized bands is quite different.
states has been shown to affect the conduction-band states over a wide (~ 40 meV) energy range in the study of Yb$_{1-x}$Lu$_x$B$_{12}$ [5.6]

![Diagram showing high-resolution photoemission spectra of YbB$_{12}$](image)

Figure 5.4: Top: High-resolution photoemission spectra of YbB$_{12}$ near $E_F$ ($h\nu = 21.2$ eV). Bottom: Spectral DOS at each temperature (thick curve) together with the DOS at 305 K (thin curve). The bottom line is the zero for the DOS at 6 K and the other densities of states have been offset.

Recently, Breuer et al. [5.22] reported the non-$f$ photoemission spectra of another Kondo insulator Ce$_3$Bi$_4$Pt$_3$ ($T_{\text{max}} \sim 80$ K and $\Delta_{\text{act}} \sim 4$ meV) in comparison with a Kondo metal CeSi$_2$. The spectrum of Ce$_3$Bi$_4$Pt$_3$ showed a shallow dip of ~ 20 meV around $E_F$ and the spectrum of CeSi$_2$ was identical to a simple Fermi edge. Very re-
5.3. Results and Discussion

Recently, it was found by Takeda et al. [5.23] that Ce$_3$Bi$_4$Pt$_3$ exhibited a sharp depression of the DOS at $E_F$ as in the present case of YbB$_{12}$. The magnitude of the depression is smaller than that of YbB$_{12}$, corresponding to the weaker temperature dependence of the electrical resistivity in Ce$_3$Bi$_4$Pt$_3$[5.24].

![DOS and Conductivity Graph](image)

Figure 5.5: Top: spectral DOS of YbB$_{12}$ at several energy positions as a function of temperature. Bottom: electrical conductivity of the same sample as a function of temperature.

In Fig. 5.5 the spectral DOS at several energies are plotted as a function of temperature and are compared with the dc electrical conductivity. All the intensities are normalized at 305 K. A decrease in the intensity from 75 K to 6 K, which is expected from the dc conductivity, is present only in the vicinity (within $\sim 10$ meV) of $E_F$. For
larger energy separation (> 20 meV) from \( E_F \), the DOS at 6 K is almost the same as or even higher than the value at 75 K. This means that in that high energy region no characteristic behavior of the Kondo insulator appears in the conduction-band spectra. Here, it should be remembered that the Kondo peak of YbB\(_{12}\) appears at \( \sim -25 \) meV [5.5], which sets a higher energy scale than the transport activation energy, and is similar to that of a Kondo metal having a similar Kondo temperature: the Kondo peak position (\( k_B T_K \)) of YbB\(_{12}\) scales with \( T_{\text{max}} \) as in metallic Kondo systems[5.25]. Thus a crossover from a Kondo metal to a Kondo insulator is expected to be observed as a function of energy separation from \( E_F \) as well as of temperature. In order to clarify the crossover, a PES study of the conduction-band states in a metallic valence-fluctuating Yb system would provide valuable information. The difference between the conduction-band states of Yb compounds and that of Ce compounds is also an important issue to be clarified in future.

### 5.4 Summary

To conclude, the temperature-dependent electronic structure of the conduction band of YbB\(_{12}\) has been studied by high-resolution PES. We have found that a sharp dip of \( \sim 10 \) meV width appears at low temperatures in addition to the broad pseudogap of \( \sim 100 \) meV, which survives at room temperature. The size of the sharp gap is consistent with the transport gap of \( \sim 12 \) meV. The missing sharp gap at high temperature is also consistent with both the high-temperature electrical resistivity and the magnetic susceptibility, where no characteristic behavior of the Kondo insulator appears.
References


References


[5.18] Application of this method to the spectra of LuB$_{12}$ would yield a temperature-independent flat DOS.

[5.19] The negative slope $d\rho/dT$ due to Kondo scattering is less commonly present in Yb compounds than in Ce compounds [e.g., D. Wohlleben and B. Wittershagen, Adv. Phys. 34, 403 (1985)].


Chapter 6

Substitution and Temperature Dependence of the Conduction Band in Yb$_{1-x}$Lu$_x$B$_{12}$

We have studied the temperature dependence of the B $p$-derived conduction band in Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0.25, 0.50, 0.75, 	ext{and} 1.00$) by high-resolution photoemission spectroscopy. As the Yb content increases, the density of states (DOS) between the Fermi level ($E_F$) and $\sim -20$ meV is depressed and simultaneously a broad peak grows at $\sim -80$ meV. Such substitution dependence is considerably weakened at higher temperature, indicating a decoupling between the $f$ electrons and the conduction electrons at high temperatures. The temperature-dependent depression near $E_F$ is abruptly enhanced for small $x$, showing an effect beyond the single-site mechanism in the gap formation of YbB$_{12}$.

6.1 Introduction

In the preceding Chapters we have shown that the gap in YbB$_{12}$ vanishes with Lu substitution (Chap. 4) [6.1] or with temperature (Chap. 5) [6.2]. In this Chapter we present the results of a thorough temperature-dependent photoemission study of the B $sp$ Yb $d$-derived conduction band in Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0.25, 0.50, 0.75, 	ext{and} 1.00$) performed on single crystals. Transport and thermodynamic properties of Yb$_{1-x}$Lu$_x$B$_{12}$ single crystals [6.3, 4] are qualitatively the same as those of polycrystals [6.5]. We show the electrical resistivity of Yb$_{1-x}$Lu$_x$B$_{12}$ single crystals [6.4] in Fig. 6.1. The activation-
type temperature dependence at low temperatures is weakened with $x$ and gradually disappears between $x = 0.25$ and $x = 0.50$. The resistivity of LuB$_{12}$ is as small as 0.13 $\mu$Ω cm at 4.2 K and rises monotonously with increasing temperature. The maximum of the magnetic susceptibility ($T_{\text{max}}$) is gradually shifted from $\sim 75$ K for YbB$_{12}$ to $\sim 100$ K for Yb$_{0.25}$Lu$_{0.75}$B$_{12}$ as shown in Fig. 6.2. The shift of $T_{\text{max}}$ would reflect an increase in the Kondo temperature ($T_K$) owing to the recovery of the conduction-band density of states (DOS) with $x$, as already discussed in Chap. 4. The suppressed magnetic susceptibility below $\sim 60$ K, which corresponds to missing Pauli paramagnetism in YbB$_{12}$, is recovered with Lu substitution.

![Figure 6.1: Electrical resistivities of Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0.00, 0.25, 0.50, 0.75, \text{and } 1.00$) single crystals [6.4].](image)

Motivation for the temperature-dependent photoemission spectroscopy (PES) study of Yb$_{1-x}$Lu$_x$B$_{12}$ is the following:

(i) Observation of systematic changes caused by the Lu substitution will give an important clue to understand whether the gap opening in YbB$_{12}$ is better described by
6.1. Introduction

Figure 6.2: Magnetic susceptibility of Yb\(_{1-x}\)Lu\(_x\)B\(_{12}\) (\(x = 0.00, 0.25, 0.50, 0.75, \) and 1.00) single crystals [6.3].

the single-site model or the itinerant picture. One can understand the mechanism of the gap opening within the single-site model if no substantial changes in the spectra appear by controlling the distances between the Kondo ions (Yb atoms) after having normalized the spectral intensities to the Yb content. In that case the depression of the spectral DOS of Yb\(_{1-x}\)Lu\(_x\)B\(_{12}\) at the Fermi level (\(E_F\)) would be simply a linear combination of the pseudogap of YbB\(_{12}\) and the Fermi edge of LuB\(_{12}\). On the other hand, the effect of coherence in the YbB\(_{12}\) lattice would appear as sensitive changes in the photoemission spectra with a smallLu substitution. Note that, in the case of FeSi, only the spectral DOS in the vicinity of \(E_F\) is sensitive to a small substitution, indicating that the coherence in the periodic lattice plays an important role in the low-energy properties of FeSi, as will be discussed in the following Chapters.

(ii) By comparing the spectra of YbB\(_{12}\) with those of the substituted samples, we can discuss details of the spectral line shape of YbB\(_{12}\). Effects of the non-periodicity and defects in the lattice at the surface prepared by scraping would be reflected in the ultraviolet photoemission spectra. One can extract intrinsic signals of YbB\(_{12}\) using the spectra of the Lu-substituted samples as references. It should be remembered that the residual DOS is observed in the photoemission spectrum of YbB\(_{12}\) at low temperature while a fully open gap is observed by tunneling spectroscopy [6.6] and optical reflectivity
(iii) The last but the most challenging motivation is to explore new electronic states near the boundary between the Kondo insulator and the Kondo metal. Note that high-temperature superconductivity emerges between the antiferromagnetic insulator and the normal metal. The electronic states in Yb$_{1-x}$Lu$_x$B$_{12}$ is worth studying because of the unusual temperature-dependent characteristics of YbB$_{12}$.

### 6.2 Experimental

The Yb$_{1-x}$Lu$_x$B$_{12}$ single crystals have been grown by floating zone method using an image furnace with four xenon lamps [6.3]. The phases of the prepared samples and included impurities have been checked by electron probe microanalysis (EPMA) and analysis of magnetic susceptibility. Residual Curie component in the magnetic susceptibility at low temperature is much reduced compared with that for polycrystals, especially in the $x = 0.50$ and 0.75 samples.

The PES measurements were performed for Yb$_{1-x}$Lu$_x$B$_{12}$ single crystals using a Scienta SES-200 analyzer and a Gammadata He discharge lamp at Hiroshima University. The experimental condition for the PES measurements was almost the same as that for the YbB$_{12}$ single crystal (Chap. 5). The base pressure in the spectrometer was $\sim 1.9 \times 10^{-10}$ Torr. We followed the measurement procedure of the YbB$_{12}$ single crystal: After scraping the samples at 300 K, we took spectra in the sequence of 300 K, 225 K, 150 K, 75 K, and 7 K without rescraping it. In the following, we present data accumulated over five or six series of such temperature-sequent measurements.

We evaporated Au on each sample to determine the Fermi level ($E_F$) and the energy resolution. The resolution was 10, 14, 14, and 8 meV for $x = 0.25$, 0.50, 0.75, and 1.00 samples. The background due to signals excited by the satellite lines has been subtracted systematically in the way described in Chap. 2.

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$^1$ Takeda et al. recalibrated the thermometer after the measurement of YbB$_{12}$ (Chap. 5), and confirmed that the room temperature was $\sim 300$ K and the reachable lowest temperature was $\sim 7$ K.
6.3 Results and Discussion

6.3.1 Substitution Dependence at 7 K

First we focus on the photoemission spectra taken at 7 K, where the effect of the Lu substitution appears clearly. The upper panel of Fig. 6.3 shows He I photoemission spectra of Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0.25, 0.50, 0.75, \text{and} 1.00$) and that of YbB$_{12}$ [6.2] taken at 7 K. All the spectra have been normalized to the integrated intensity below $-200$ meV. In the lower panel of the figure, we have subtracted the spectrum of LuB$_{12}$ from those of Yb$_{1-x}$Lu$_x$B$_{12}$ ($x = 0.00, 0.25, 0.50, \text{and} 0.75$). In going from LuB$_{12}$ to YbB$_{12}$, the intensity of the broad peak around $-80$ meV develops whereas the intensity between $E_F$ and $-30$ meV is reduced. The energy position of the broad peak is almost independent of the Lu content.

In the band-structure calculation of YbB$_{12}$ [6.8], the boron $p$ partial DOS near the Yb $4f$ peak is modulated due to hybridization with the Yb $4f$ states as shown in Fig. 6.4: A sharp peak appears at $\sim 0.1$ eV above the Yb $4f$ level and a broad shoulder appears at $\sim 0.4$ eV below the $f$ level. The broad peak around $-80$ meV in the photoemission spectra would correspond mainly to the latter structure of the conduction band caused by the B $p$ - Yb $f$ hybridization. The reduction of the energy scale compared to the band-structure calculation would be due to electron correlation within the Yb $4f$ band. That is, the Yb $4f$ peak is located at $\sim -25$ meV in the photoemission spectra whereas the calculated Yb $f$ DOS extends from $\sim -0.1$ eV to $\sim -0.4$ eV (Chap. 3). Also, that the effective Yb $f$ - B $p$ hybridization strength has been reduced by the electron correlation at the Yb site leads to another deviation from the band-structure calculation. On the other hand, no trace of the B $p$-derived sharp peak predicted by the band-structure calculation is observed in the difference spectra in the lower panel of Fig. 6.3. The B $p$-derived sharp peak might be largely located above $E_F$.

The spectra near $E_F$ is shown in the upper panel of Fig. 6.5 on an enlarged energy scale. In the lower panel we show the photoemission spectra of the polycrystals taken at $\sim 30$ K with resolution of 21-25 meV, normalized to the integrated intensity between $-200$ meV and $-260$ meV as done for the spectra of the single crystals\footnote{In Chap. 4 we have normalized the He I spectra of Yb$_{1-x}$Lu$_x$B$_{12}$ to the intensity around $-100$ meV to discuss only the vicinity of $E_F$.}. Note that the spectra for the single crystals were taken at lower temperature and with higher
Figure 6.3: Upper panel: Photoemission spectra of $\text{Yb}_{1-x}\text{Lu}_x\text{B}_{12}$ at 7 K. Lower panel: Difference between the spectra of $\text{Yb}_{1-x}\text{Lu}_x\text{B}_{12}$ and that of $\text{LuB}_{12}$. They have been smoothed since the statistical noise of the raw difference spectra was rather high.
6.3. Results and Discussion

Figure 6.4: Calculated Yb $f$ and B $p$ partial DOS of YbB$_{12}$ [6.8] and B partial DOS of LuB$_{12}$ [6.9], where the $f$ structure are located $\sim$ 4 eV below $E_F$. We have shifted 0.57 eV the B $p$ partial DOS of LuB$_{12}$ to show the effect of the Yb $f$ - B $p$ hybridization on the B $p$ DOS.

instrumental resolution. Also, as already mentioned for Fig. 5.1 and Fig. 5.2, the sample quality was improved in the single crystals. It is common to the poly- and single- crystal spectra that with Lu substitution the spectral weight between $E_F$ and 20 meV below it increases while that below $\sim$ 30 meV decreases corresponding to the decrease in the intensity of the $\sim$ 80 meV peak.

6.3.2 Conduction Band in LuB$_{12}$

Here we discuss the conduction band in the reference compound LuB$_{12}$ and its temperature dependence. The upper panel of Fig. 6.6 shows temperature-dependent He I spectra of LuB$_{12}$. The spectra have been normalized to the integrated intensity below $\sim$ 200 meV as done for the spectra of YbB$_{12}$ in Chap. 5. The increase in the spectral weight above $E_F$ in going 7 K to 300 K is obviously larger than the decrease below $E_F$, indicating a temperature dependence other than the effect of the Fermi-Dirac (FD)
Figure 6.5: Photoemission spectra of Yb$_{1-x}$Lu$_x$B$_{12}$ taken at 7 K on an enlarged energy scale (upper panel). The spectra of polycrystals taken at $\sim$ 30 K with energy resolution of 21-25 meV is also shown in the lower panel. Normalization of the spectra is the same as in Fig. 6.3.
distribution function. Thus we again divided the spectra by the FD function (convoluted with a Gaussian corresponding to the energy resolution) as shown in the lower panel of the figure. The spectral DOS thus obtained is found to increase with increasing temperature in a rather wide energy region between $E_F$ and $\sim -100$ meV.

![Intensity and DOS of LuB$_{12}$](Image)

Figure 6.6: Temperature-dependent He I photoemission spectra of LuB$_{12}$ (upper panel) and those divided by the FD function convoluted with the instrumental resolution (lower panel).

We note again that the intensity at $E_F$ in the spectra divided by the convoluted FD function does not depend on uncertainties in the temperature nor the Gaussian width, because the FD function is 0.5 at $E_F$ at any temperature even if that FD function is convoluted with any Gaussian. However, an error in the temperature or the Gaussian width might cause a spurious temperature dependence near $E_F$ in the FD-function-divided spectra. The fact that temperature dependence is more remarkable
at about $-10$ meV than at $E_F$ in the FD-function-divided spectra might lead one to doubt the calibration of the temperature, the Gauss width, and/or the background signal which is caused by excitation of the satellite resonance lines. Therefore, we have deduced the spectral DOS of LuB$_{12}$ using another method as shown in Fig. 6.7; where we have reversed the energy scale of a spectrum with respect to $E_F$ and added it to the original spectrum [6.10]. For this method, precise information about the measurement temperature and the instrumental resolution is not needed$^3$ while asymmetry between the occupied and unoccupied states is neglected. This analysis has revealed again the increase in the spectral DOS with temperature between $E_F$ and $-100$ meV and the strongest temperature dependence occurring at $\sim -10$ meV rather than at $E_F$. Nevertheless, the temperature dependence of the spectral DOS of LuB$_{12}$ and that of YbB$_{12}$ is qualitatively different: The sharp depression of the DOS at $E_F$ is present in YbB$_{12}$ but is absent in LuB$_{12}$.

![Figure 6.7: Temperature-dependent spectral DOS deduced by adding the photoemission spectra and “reversed” spectra. For each sample, $T = 7$ K (thick curve), 75 K, 150 K, 225 K, and 300 K from bottom.](image)

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$^3$ Also, the slope of the background is cancelled in this method.
Apart from the temperature dependence, the line shape of the spectral DOS itself is also unexpected. Band-structure calculation for LuB$_{12}$ [6.9] has given a DOS of a weakly positive slope as shown in Fig. 6.8, which is almost flat around $E_F$ on the energy scale discussed here. On the other hand, the spectral DOS shows a strongly negative slope.

![Figure 6.8: Calculated B $p$ and Lu $d, f$ partial DOS of LuB$_{12}$ [6.9].](image)

In the FD-function-divided spectra, we can also study part of the unoccupied states. In the lower panel of Fig. 6.6, the slope of the spectral DOS at higher temperature around and above $E_F$ is zero or positive, different from that below $E_F$. To understand the discrepancy between the photoemission spectra and the band-structure calculation as well as the unusual temperature dependence of the spectral DOS, we can assume a V-shaped spectral DOS in LuB$_{12}$ as the simplest scenario: Since electron correlation would be important also in the B $sp$ band, the spectral DOS at $E_F$ may be suppressed in comparison with the DOS calculated within the one-electron approximation. At higher temperature, the sharp cusp-like spectral DOS at $E_F$ would be gradually smeared out due to various temperature-induced excitations including phonons.

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4 The extrapolated linear DOS crosses the base line at 170 meV above $E_F$, too inclined to compare with the calculated DOS.
6.3.3 Substitution and Temperature Dependence

Figure 6.9: Spectral DOS of Yb$_{1-x}$Lu$_x$B$_{12}$ deduced by dividing the spectra by the FD function. The base line is for the spectral DOS of LuB$_{12}$ and other DOS are offset. For each composition, $T = 7$ K (thick curves), 75 K, 150 K, 225 K, and 300 K from bottom.

Hereafter we deal with the spectral DOS deduced by dividing the He I spectra by the FD function. The temperature-dependent spectral DOS of Yb$_{1-x}$Lu$_x$B$_{12}$ and those of YbB$_{12}$ are shown in Fig. 6.9. Although the substitution effect on YbB$_{12}$ is present noticeably in the raw data taken at 7 K, it appears more clearly in the temperature dependence of the spectral DOS at various energies as presented in Fig. 6.10. The spectral DOS of LuB$_{12}$ also shows a temperature dependence, but its DOS is uniformly depressed while the DOS of Yb-rich samples shows a stronger depression in the vicinity
of $E_F$. Under this normalization, the DOS at $-50$ meV and $-80$ meV are almost identical and both decrease slightly on cooling for all samples.

![Temperature-dependent DOS of Yb$_{1-x}$Lu$_x$B$_{12}$ at various energies. We have re-normalized the DOS to the values at 300 K.](image)

Figure 6.10: Temperature-dependent DOS of Yb$_{1-x}$Lu$_x$B$_{12}$ at various energies. We have re-normalized the DOS to the values at 300 K.

We subtracted the DOS at 7 K from those at 300 K for each $x$ in Fig. 6.11. As is visible in Fig. 6.9, the depressed DOS is always positive under the normalization in Fig. 6.9. At $-80$ meV, the depressed DOS decreases as Yb content increases corresponding to the evolution of the broad peak. The $x$ dependence at $-50$ meV is substantially the same as that at $-80$ meV. The depression is much stronger at $-20$ meV but its response against $x$ resembles that at $-50$ meV and $-80$ meV. However, the $x$ dependence at $E_F$ is qualitatively different from those below $-20$ meV: The depression at $E_F$ is identical to that at $-20$ meV for $x \geq 0.5$ but the depression at $E_F$ is remarkably enhanced for $x \leq 0.25$. This indicates that the sharp (pseudo)gap, which opens less than 20 meV from $E_F$ and governs the low-temperature transport and thermodynamic properties of YbB$_{12}$, disappears between $x = 0.25$ and 0.50. Such a nonlinear response at $E_F$ against $x$ would suggest that the effect beyond the single-site mechanism plays an important role in the low-energy electronic properties in YbB$_{12}$. 
including a formation of the narrow gap.

On the other hand, the larger pseudogap of \( \sim 0.1 \) eV does not show even a linear \( x \)-dependence, indicating that it is principally the electronic structure in LuB\(_{12}\) and is not strongly deformed by the existence of the Yb 4f states. Near \( E_F \), the depression of the larger pseudogap with temperature is stronger, but its \( x \) dependence is qualitatively different from that at \( E_F \).

![Figure 6.11: Depression in the spectral DOS in going 300 K to 7 K, plotted against the Lu content. The DOS values have been read from Fig. 6.9, not from Fig. 6.10](image)

In order to extract the effect of Lu substitution, we have subtracted the 7 K spectral DOS of LuB\(_{12}\) from all the other spectral DOS as shown in Fig. 6.12. Figure 6.12 (a) exhibits the temperature dependence of the difference DOS for each sample. The depression of the DOS at \( E_F \) in going from 300 K to 7 K occurs almost in the same way for \( x = 1.00, 0.75, \) and 0.50 samples although the DOS at each temperature is slightly lowered in going from \( x = 1.00 \) to 0.50 as shown in Fig. 6.12 (b). The depression at \( E_F \) in going from 300 K to 7 K is enhanced for \( x = 0.25 \) and 0.00 and a simple linear interpolation of the DOS at \( E_F \) between \( x = 0.00 \) and \( x = 1.00 \) does not represent
the DOS at $E_F$ for Yb$_{1-x}$Lu$_x$B$_{12}$. This substitution dependence of the depression is consistent with the results of the electrical resistivity, the specific heat, and the magnetic susceptibility, where the insulating behavior survives up to $x \sim 0.5$ but disappears for $x > \sim 0.5$.

On the other hand, the broad peak around $\sim -80$ meV, which has been revealed in Fig. 6.3, appears even for $x = 0.75$ and the peak position is independent of the Yb content. In contrast to the suppressed DOS at $E_F$, the peak appears to grow in proportion to the Yb content, probably due to the hybridization between the B $sp$ and the Yb 4$f$ states at the Yb sites. We note that the temperature dependence of the DOS of LuB$_{12}$ extends up to $\sim -150$ meV, where the DOS of other samples does not show temperature dependence. Thus the temperature dependence extending up to $\sim -150$ meV might be compensated with the spectral-weight transfer from around $E_F$ to the broad peak in the samples containing Yb atoms.

It should be reminded again that the He I spectra probe the B $sp$ - Yb $d$-derived conduction-band states and not the Yb 4$f$-derived states. Therefore, the integrated He I spectral DOS can change with temperature if the Yb 4$f$ - B $sp$ hybridization changes with temperature, although the total spectral DOS integrated over a sufficiently wide energy range should be conserved at different temperatures. Rozenberg et al. [6.11] calculated the temperature dependence of the DOS of both 4$f$- and conduction-electrons by mapping the periodic Anderson model onto an effective local impurity model, i.e., by solving the periodic Anderson model within dynamical mean-field theory. A dip appears in the conduction-band DOS at low temperature and the integrated conduction-band DOS with 10 times the gap size decreases clearly on cooling. On the other hand, a gap sandwiched by sharp peaks evolves in the 4$f$ DOS at low temperature and the integrated 4$f$ DOS increases on cooling.

The substitution dependence appears most clearly at 7 K as shown in the bottom panel of Fig. 6.12 (b). However, such substitution dependence is smeared out at higher temperatures. This is contrasted with the spectral DOS of FeSi$_{1-x}$Al$_x$, which is discussed in Chap. 8. Note that the temperature scale observed in the transport and thermodynamic properties is much larger in FeSi. Gradual disappearance of the substitution dependence at higher temperatures would indicate that the 4$f$ electrons are decoupled with the conduction electrons in going through $T_K \sim 220$ K [6.12]. In Chap. 4 we have revealed that the Kondo peak is shifted by about 10 meV in going from YbB$_{12}$ to Yb$_{0.5}$Lu$_{0.5}$B$_{12}$. Thus a 4$f$ photoemission study of these single crystals
Chapter 6. Substitution and Temperature Dependence of the Conduction ...

Figure 6.12: (a) Difference spectral DOS of $\text{Yb}_{1-x}\text{Lu}_x\text{B}_{12}$ relative to the spectral DOS of $\text{LuB}_{12}$ at 7 K. All the DOS have been smoothed to the same extent. For each $x$, $T = 7$ K (thick curves), 75 K, 150 K, 225 K, and 300 K from bottom. (b) The same difference DOS as (a) showing the substitution dependence at each temperature. The thick solid curves represent the DOS of the $x = 0$ sample, the dashed curves $x = 0.25$, the solid curves $x = 0.50$, the dot-dashed curves $x = 0.75$, and the solid dashed curves $x = 1.00$. 

Energy relative to $E_F$ (meV)
and consistent analysis of both the $4f$ and conduction-band spectra would be highly desirable in future.

6.4 Summary

We have studied the Lu-substitution dependence in the photoemission spectra of the $Bsp$-derived conduction band in $\text{Yb}_{1-x}\text{Lu}_x\text{B}_{12}$ at various temperatures. The substitution dependence is most clearly present at 7 K, where in going from LuB$_{12}$ to YbB$_{12}$ the pseudogap of $< 20$ meV opens and a broad peak at $\sim - 80$ meV evolves. Such substitution dependence is gradually smeared out with increasing temperature, indicating a decoupling between the $f$ electrons and the conduction electrons above $\sim T_K$. The larger pseudogap of 0.1 eV, which has been observed in YbB$_{12}$, is present for any $x$ concentration including LuB$_{12}$ but the sharp depression in the vicinity of $E_F$ is observed only for $x \leq 0.25$. That the spectra for intermediate $x$'s cannot be reproduced by a $1 - x : x$ superposition of those of YbB$_{12}$ and LuB$_{12}$ indicates that the effect beyond the single-site description is important in the gap formation of YbB$_{12}$. 
References


Chapter 7

Temperature and Co-Substitution Dependence of the Photoemission Spectra of FeSi

We have studied the effect of varying temperature and Co substitution on the low-energy electronic structure of FeSi by photoemission spectroscopy. We have observed that the density of states (DOS) of FeSi is reduced at low temperatures over a wide energy range of \( \sim 50 \) meV below the Fermi level \((E_F)\), which is the energy scale observed by the magnetic, transport and optical measurements. The reduced DOS is completely recovered with increasing temperature but only partly, i.e., predominantly near \( E_F \), with Co substitution, again consistent with the transport properties.

7.1 Introduction

Among various transition-metal compounds, FeSi shows unique magnetic and transport properties which are sometimes discussed in connection with the characteristics of narrow-gap \( 4f \)-electron systems or Kondo insulators [7.1]. At low temperatures FeSi is a nonmagnetic semiconductor. With increasing temperature the magnetic susceptibility rises exponentially to reach a broad maximum at \( \sim 500 \) K and follows a Curie-Weiss law at higher temperatures [7.2]. The electrical resistivity falls more than three orders of magnitude with increasing temperature up to \( \sim 300 \) K [7.3] but rises slowly above \( \sim 300 \) K like a metal. In recent years, the temperature-dependent electronic structure of FeSi has been studied extensively by spectroscopic methods [7.4–14]. Schlesinger
et al. [7.4] performed the first optical study of FeSi and found that the optical gap of \( \sim 60 \) meV was opened below \( \sim 200 \) K, a rather low temperature compared with the gap size as presented in Fig. 7.1. This gap is confirmed by Degiorgi et al. [7.11] and Damascelli et al. [7.13] although the energy range of spectral weight redistribution remains controversial. Nyhus et al. [7.14] reported that at low temperatures the Raman intensity centered at \( \sim 100 \) meV grows simultaneously with decreasing intensity below \( \sim 60 \) meV.

While the optical conductivity is due to direct transitions between the occupied and unoccupied states, photoemission spectroscopy (PES) involves only the occupied states. Thus PES studies are expected to yield less ambiguous information on the unusual electronic structure of FeSi. However, even more puzzling results have come out from recent PES studies: two angle-integrated PES studies showed no temperature dependence of the spectra beside a small shift away from the Fermi level \( (E_F) \) [7.6, 7]. That is, Chainani et al. [7.6] and Saitoh et al. [7.7] compared spectra taken at different temperatures and concluded that a gap as small as \( \sim 5 \) meV is opened at low temperatures, which energy scale does not appear in any other measurements. An angle-resolved photoemission study by Park et al. [7.9] revealed a narrow band dispersing by \( \sim 30 \) meV, indicating a strong correlation in FeSi. Saitoh et al. [7.7] attributed the difference between the angle-integrated photoemission spectra of FeSi and the band-structure density of states (DOS) [7.15] to the self-energy correction and concluded that near \( E_F \) a strong band narrowing is present, consistent with the angle-resolved study. Note that the dispersion of every energy band in FeSi is larger than \( \sim 300 \) meV in the band structure calculations [7.15, 16]. Very recently, Breuer et al. [7.8] performed a partially angle-integrated photoemission study of single crystalline FeSi with higher energy resolution and found that the spectral intensity decreases between \( E_F \) and 40 meV below it at low temperatures, consistent with the energy scale seen in the optical conductivity. They also stated that a full gap at \( E_F \), if existed at all, would be less than 1 meV.

In this work, in order to further clarify the electronic structure of FeSi, we have studied detailed temperature dependence as well as the effect of Co substitution for Fe by high-resolution angle-integrated photoemission measurements. Because comparison of high-resolution spectra taken at different temperatures is rather difficult owing to the strong temperature dependence of the Fermi-Dirac distribution function, we have attempted to remove that effect and to extract the intrinsic temperature dependence
Figure 7.1: Infrared reflectivity $R$, optical conductivity $\sigma_1(\omega)$, and the integral of $\sigma_1(\omega)$ from 0 to $\omega$, $n(\omega)/m^*$ for FeSi at 20 K (solid curves), 100 K (dashed curves), 150 K (dots), 200 K (dot-dashed curves), and 250 K (solid curves). The inset in panel (c) shows the difference between $n(\omega)/m^*$ at 250 K and at 20 K (solid curve). The dotted curve has been deduced by shifting the 20 K reflectivity by 0.5 % to show the accuracy [7.4].
of the spectral DOS, i.e., the $k$-integrated spectral function.

### 7.2 Experimental

![Graph showing electrical resistivities of FeCo$_{1-x}$Si$_x$ polycrystals](image)

Figure 7.2: Electrical resistivities of FeCo$_{1-x}$Si$_x$ polycrystals [7.19].

The Fe$_{1-x}$Co$_x$Si alloys form a solid solution of the B20-type cubic structure in the whole concentration range. They become conductive as Co is substituted and gradually become metallic for $x \geq 0.05$. They show weak ferromagnetism or helical spin order for $0.05 < x < 0.80$. The transition temperature is rather low, 21.3 K and the ordered moment is small, $< 0.1 \, \mu_B$ for $x = 0.10$ [7.18]. The low-temperature Hall coefficient of Fe$_{1-x}$Co$_x$Si changes its sign from negative to positive as $x$ increases although Co substitution for Fe nominally corresponds to electron doping [7.19]. This means that the effect of Co substitution is not simply a rigid-band shift of $E_F$. In the present work, we concentrate on the low Co-concentration regime. Polycrystalline samples of FeSi, Fe$_{0.95}$Co$_{0.05}$Si and Fe$_{0.90}$Co$_{0.10}$Si were prepared by arc-melting Fe, Co and Si in an argon atmosphere. A slightly excess Si was incorporated to avoid a mixing of magnetic impurities of Fe or Co. The prepared samples were checked by x-ray diffraction. The resistivity of Fe$_{1-x}$Co$_x$Si is presented in Fig. 7.2. As Co is substituted, a metallic temperature dependence appears in the low-temperature resistivity. As the photoemission
light source we used the He I resonance line ($h\nu = 21.2$ eV). The samples were repeatedly scraped in an ultra-high vacuum with a diamond file to obtain fresh surfaces. The base pressure of the spectrometer was in the $10^{-11}$ Torr range. The Fermi edge of Au film evaporated on the sample surface after each series of measurements was used to determine $E_F$ and the instrumental resolution. The resolution thus determined was $\sim 20$ meV.

### 7.3 Results and Discussion

![Figure 7.3: Entire valence-band photoemission spectra of Fe\(_{1-x}\)Co\(_x\)Si taken with $h\nu = 21.2$ eV.](image)

Figure 7.3 shows the entire valence band of Fe\(_{1-x}\)Co\(_x\)Si. As already reported [7.6, 7], the temperature dependence of the photoemission spectra of FeSi in such a wide energy scale is negligible. Also, Fig. 7.3 shows that the spectra do not change for
a small amount of Co substitution on this energy scale. Figure 7.4 shows changes induced by Co substitution near $E_F$. We have subtracted the spectra of pure FeSi from those of Co-substituted samples as shown in the lower panel. The obtained difference spectra indicates that the DOS around $E_F$ in FeSi is increased upon Co substitution, corresponding to the substitution-induced metallic behavior. Apart from the vicinity of $E_F$ there is no clear structure in the difference spectra. We also note that the position of the broad peak at $\sim -0.3$ eV in pure FeSi is shifted by $\sim 0.1$ eV towards higher binding energy in the Co-substituted samples.

The temperature dependence of the spectra near $E_F$ is presented in Fig. 7.5. Normalized at higher binding energies ($< -0.1$ eV), the midpoint of the leading edge in FeSi appears to be shifted by $\sim 5$ meV away from $E_F$ at low temperatures as reported previously [7.6, 7], clearly different from the spectra of Au shown in the same figure. The temperature-dependent spectra of Fe$_{1-x}$Co$_x$Si show a similar shift of the leading
edge. However, the edge at 18 K appears again closer to $E_F$ than that at 75 K, questioning the simple interpretation of the leading edge shift with temperature. Another possibility is a reduction of the DOS at $E_F$ with decreasing temperature, which could lead to the apparent shift of the leading edge as observed experimentally. The difficulty to distinguish between the two possible scenarios of the spectral changes with temperature comes from the difficulty to extract changes in the DOS itself apart from the temperature dependence of the Fermi-Dirac distribution function. Therefore, we have divided the photoemission spectra by the Fermi-Dirac distribution function (convoluted with a Gaussian corresponding to the instrumental resolution) [7.20]. This method gives reliable results in cases where the DOS has only broad structures near $E_F$: application of this method to the spectra of Au yields a reasonably flat DOS as shown in the

Figure 7.5: Photoemission spectra of FeSi, Fe$_{0.9}$Co$_{0.1}$Si and Au taken at different temperatures.
lowest panel of Fig. 7.6.\(^1\) The spectral DOS thus obtained for FeSi and Fe\(_{1-x}\)Co\(_x\)Si are shown in Fig. 7.6. One can see that the energy range where the DOS vary with temperature is between \(E_F\) and \(\sim 50\) meV below it, consistent with the data taken at room temperature and \(\sim 10\) K reported by Breuer et al. [7.8] The size of this wide dip or “pseudogap” is almost independent of the Co content. The pseudogap is wide enough compared with the instrumental resolution and therefore the present approach of dividing the spectra with the Fermi-Dirac distribution function is valid to discuss this structure. From the present PES spectra, however, one cannot conclude where the missing spectral weight in the pseudogap region is transferred. Here, it should also be noted that spectral weight around \(E_F\) remains substantially high at all temperatures, contrasted with the optical conductivity data, in which almost all the spectral weight is depleted below \(\sim -60\) meV at low temperatures. Comparing the data from single crystals and polycrystals, Breuer et al. [7.8] proposed that the surface might be metallic and contribute the observed spectral weight at and around \(E_F\).

In Fig. 7.6 we note that the recovery of the DOS with temperature and with Co substitution is dependent on the energy position: we show in Fig. 7.7 the temperature dependence of the DOS at \(E_F\) and 30 meV below it. Plotted are the intensities relative to the values at room temperature. The DOS at \(E_F\) of pure FeSi increases with temperature more rapidly than those of Co-substituted samples. On the other hand, such a difference between the pure and Co-substituted samples is absent at \(-30\) meV. This has already been suggested in Fig. 7.4, which shows that the Co substitution affects mainly the vicinity of \(E_F\). Here, we note that the recovery of the spectral function both at \(E_F\) and 30 meV below it starts between 225 K and 150 K, low enough temperatures compared with the gap size. This is consistent with the temperature dependence of the optical conductivity, where the gap feature disappears above \(\sim 200\) K. The bottom panel of Fig. 7.7 shows the dc conductivity of the samples studied here normalized to the values at room temperature. (The room-temperature conductivity of pure FeSi is \(\sim 75\%\) of those of the \(x = 0.05\) and \(x = 0.10\) samples.) Like the DOS at \(E_F\), the dc conductivity depends on Co content mainly below \(\sim 200\) K. Thus we can state

\(^1\) On the other hand, one cannot discuss sharp structures compared with the energy resolution from these DOS thus obtained although sharp structures sometimes appear as spurious features. We have made extensive simulations for various DOS line shapes and temperatures in order to see to what extent the present method is reliable in extracting the original DOS. Figure 7.6 indicates temperature-dependent spectral changes in the wide energy range but from this figure alone one cannot exclude the possibility that a sharp gap compared with the energy resolution is opened near \(E_F\).
that the low-energy (< 30 meV) or low-temperature (< 200 K) electronic structure is strongly affected by the small amount of Co substitution in contrast to the high-energy or high-temperature electronic structure. This is consistent with the recent transport and optical study of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ [7.21]: the gap size deduced from the optical conductivity and the high-temperature (130 < $T$ < 300) dc conductivity is independent of the small content of Co substitution of 0 ≤ $x$ ≤ 0.02 although only $x = 0.005$ substitution of Co drastically varies the dc conductivity below 90 K.

As already mentioned, the broad peak at 0.2-0.3 eV below $E_F$ may be another key feature to understand the electronic structure of FeSi in connection with the hybridization gap model of the Kondo insulators, where extended conduction bands (Fe 3$d$-Si 3$p$ bonding bands, in the present case) hybridize with localized $d$ bands (nonbonding Fe
Figure 7.7: Top and middle panels: temperature-dependent spectral DOS at $E_F$ and 30 meV below it as deduced from Fig. 7.6. Bottom: electrical conductivity of Fe$_{1-x}$Co$_x$Si [7.19].

$3d$ bands), leading to a modulation of the conduction-band DOS and a gap sandwiched by high DOS$^2$. Recalling that the observed spectra mainly come from transition-metal $3d$ states [7.22], Co substitution for Fe necessarily leads to changes in the broad peak corresponding to the appearance of Co $3d$ states even if the physical properties are not much influenced by the substitution$^3$. Photoemission studies on FeAl$_x$Si$_{1-x}$ and FeSi$_{1-x}$P$_x$, in which the Fe atoms are not substituted, would give clearer information on the relationship between the collapse of the insulating behavior and the change in the broad peak.

$^2$ In Chap. 4 we have presented the recovery of DOS at $E_F$ accompanied by the shift of the Kondo peak position away from $E_F$ in Yb$_{1-x}$Lu$_x$B$_{12}$

$^3$ Son et al. measured photoemission spectra of Fe$_{0.5}$Co$_{0.5}$Si and found the peak at $\sim -0.7$ eV [7.23].
7.4 Summary

To conclude, we have measured photoemission spectra of Fe$_{1-x}$Co$_x$Si and discussed their temperature and $x$-dependences in comparison with the optical conductivity and the dc conductivity. At low temperatures, the spectral DOS of FeSi show a pseudogap of $\sim$ 50 meV width, almost equal to the gap size observed in the optical measurements. The pseudogap disappears above $\sim$ 200 K, consistent with the temperature dependence of the optical conductivity. Co substitution affects low-temperature and low-energy electronic structure of FeSi and recovers the DOS in the vicinity of $E_F$, in parallel with the changes in the dc conductivity.
References


Chapter 8

Temperature and Al-Substitution Dependence of the Photoemission Spectra of FeSi

We have performed temperature-dependent high-resolution photoemission measurements on FeSi$_{1-x}$Al$_x$ ($x = 0.00, 0.02, 0.05, 0.10,$ and $0.30$) and have identified three different energy regions near the Fermi level ($E_F$) from the different responses of the spectral density of states (DOS) to temperature and Al substitution. That is, the dip in the vicinity ($\sim 20$ meV) of $E_F$ which is sensitive to a small amount of Al substitution and a small temperature increase, the pseudogap region ($\sim 50$ meV) whose depth smoothly depends on Al substitution and temperature, and the shoulder near the valence-band top ($\sim 100$ meV), which grows with decreasing Al concentration in going from $x = 0.30$ to 0.00. The broad peak at $\sim 400$ meV below $E_F$ is stable against both temperature and substitution unlike that in Fe$_{1-x}$Co$_x$Si, where the peak position moved for a small amount of Co substitution.

8.1 Introduction

In the preceding photoemission study of FeSi, we have found that Co substitution recovers the density of states (DOS) in the vicinity of the Fermi level ($E_F$) and does not modify the size of the pseudogap of $\sim 50$ meV. The broad peak at $\sim -0.3$ eV also depends on the substitution and is shifted to higher binding energies with Co substitution. However, although Co substitution increases the band filling in FeSi, it
was difficult to distinguish between the intrinsic effect of changes in the band filling on the spectral DOS of FeSi and the difference in the 3\textit{d} levels of Fe and Co. Photoemission spectroscopy (PES) measurements of Si-site substituted samples would enable one to extract the effect of changes in the band filling and to discuss the origin of both the pseudogap around \(E_F\) and the broad peak at \(\sim 0.3\) eV below \(E_F\).

Figure 8.1: Hall resistance of FeSi\(_{1-x}\)Al\(_x\). Carrier concentration calculated from \(R_H\) at 4 K is shown in the inset [8.11].

Transport and thermodynamic properties of FeSi\(_{1-x}\)Al\(_x\) (0 \(\leq x \leq 0.08\)) have been studied by DiTusa et al. [8.10, 11]. Figure 8.1 shows the Hall resistance (\(R_H\)) of FeSi\(_{1-x}\)Al\(_x\) for 0.00 \(\leq x \leq 0.08\). Carrier concentration calculated from \(R_H\) at 4 K, which is shown in the inset, indicates that Al substitution donates one hole per added Al in the samples. They concluded from the critical behavior of conductivity near the metal-insulator transition (\(\sigma = \sigma_0[(n/n_c) - 1]^{\nu}\)) that apart from the strongly renormalized mass, the metallic behavior of doped FeSi \((x \geq 0.01)\) is basically the same as that of a doped band insulator in the same sense that the heavy fermion metal is a Fermi liquid with a greatly enhanced band mass.

It should be remembered that in YbB\(_{12}\) some higher-energy structures exist in the spectral DOS other than the (pseudo)gap at \(E_F\) which agrees with the transport activation energy: They are a large pseudogap, which is larger than the transport gap, the Kondo peak, and a broad peak in the conduction band DOS. In addition to the similarities between FeSi and the 4\textit{f}-electron Kondo insulator pointed out by Aeppli
and Fisk [8.2] for the first time, we stress another similarity between FeSi and YbB$_{12}$ that almost non-dispersing bands exist just below $E_F$ [8.4]. In the band structure of FeSi calculated by Mattheiss and Hamann [8.3], a band located just below the gap has a very small dispersion of a few tens meV along the $\Gamma X$, $\Gamma M$, and $\Gamma R$ directions. This is in contrast with the conduction bands just above $E_F$, which are moderately dispersing. The narrow band on the occupied side in FeSi has been observed in recent angle-resolved PES studies [8.5, 6].

Angle-integrated PES studies of FeSi have revealed an opening of the pseudogap of 40-50 meV [8.7, 9] with a finite spectral weight at the bottom of the pseudogap. The depression of the spectral DOS in FeSi is not so sharply dipped as that in YbB$_{12}$ and thus the spectral weight at $E_F$ would remain finite even if the broadening due to instrumental resolution has been removed. Breuer et al. [8.7] stated based on their high-resolution ($\Delta E \sim 5$ meV) photoemission data that a full gap at $E_F$, if opens, should be less than 1 meV.

In this work, we have made a detailed study of substitution effect on the electronic structure of FeSi. Systematic substitution effects have been observed not only in the pseudogap around $E_F$ but also on a higher energy scale, which was not possible to identify in the spectra of Fe$_{1-x}$Co$_x$Si because of the differences between Fe 3$d$- and Co 3$d$-related structures.

### 8.2 Experimental

FeSi$_{1-x}$Al$_x$ ($x = 0.00, 0.02, 0.05, 0.10,$ and 0.30) polycrystals were prepared by arc melting Fe, Si, and Al in an argon atmosphere [8.8]. An excess Si and Al of $\sim 5\%$ was incorporated in the starting stoichiometry. The samples were checked to be single phases by powder x-ray diffraction analysis. The electrical resistivity of the prepared samples are shown in Fig. 8.2 [8.8]. The $x = 0.02, 0.05,$ and 0.10 samples exhibit semiconducting behavior above the resistivity maxima at $\sim 35$ K, $\sim 70$ K, and $\sim 95$ K, respectively, with almost the same activation energy as that of pure FeSi [8.8]. At lower temperature, the resistivity decreases on cooling down as in a metal. The resistivity of the $x = 0.30$ sample decreases monotonously on cooling below room temperature.

We have performed PES measurements on these samples using a newly developed PES systems with a VG He lamp and an Omicron EA 125 HR analyzer. The advantage of this system compared with the previous one, which was used for the measurements
of Fe$_{1-x}$Co$_x$Si, is (i) the extended measurement temperature range down to 7 K, (ii) the improved pressure in the spectrometer, and (iii) the higher energy resolution. The sample surface was scraped in the ultrahigh vacuum. The base pressure was in the 10$^{-11}$ Torr range and remained in the 10$^{-10}$ Torr range even with the He lamp working, which is 10 times better than that of the previous system. We evaporated Au on the measured samples to determine the Fermi level ($E_F$) and the instrumental resolution. The energy resolution for He I spectra was 14-16 meV. The satellite lines are much weak compared with the He I line for the VG lamp, but before dividing the spectra by the Fermi-Dirac (FD) function we have subtracted the background systematically following the procedure described in Chap. 2 to deal with a slight change in the spectral DOS.

Figure 8.2: Electrical resistivities of FeSi$_{1-x}$Al$_x$ polycrystals [8.8].
8.3 Results and Discussion

Figure 8.3: Photoemission spectra of FeSi$_{1-x}$Al$_x$ taken with He II. A rise below $\sim -7$ eV in the $x = 0.02$ spectrum might be due to signal from a Cu plate on which the sample is mounted since the size of the $x = 0.02$ sample was comparable to the spot size of the He lamp.

Figure 8.3 shows He II spectra of FeSi$_{1-x}$Al$_x$ in a wide energy range$^1$. The valence band of FeSi$_{1-x}$Al$_x$, including that of FeSi$_{0.70}$Al$_{0.30}$, is almost identical with that of FeSi.

Substitution dependence appears in the high-resolution He I spectra shown in Fig. 8.4. The spectra have been normalized to the intensity below $-0.4$ eV. We have subtracted

$^1$ In the case of Fe$_{1-x}$Co$_x$Si, He II ($h\nu = 40.8$ eV) spectra agreed with He I ($h\nu = 21.2$ eV) spectra. He I spectra below $\sim -8$ eV, where the kinetic energy of emitted photoelectrons is rather low, were not perfectly reproducible using the Omicron analyzer and thus we used the He II line to observe the entire valence band.
Chapter 8. Temperature and Al-Substitution Dependence of the...

Figure 8.4: Photoemission spectra of FeSi$_{1-x}$Al$_x$ taken at 7 K (a) and at 295 K (b). Difference spectra between FeSi$_{1-x}$Al$_x$ and FeSi are shown in the lower panels.

the spectra of FeSi from those of FeSi$_{1-x}$Al$_x$ as shown in the lower panels of Fig. 8.4 (a) and (b). The change in the spectra with Al substitution is 4 % at 7 K and reaches 7 % at 295 K. Also, the substitution dependence appears in wider energy region at 295 K. Spectral weight in the whole energy region between $E_F$ and $-300$ meV is reduced with substitution at 295 K. Such a decrease with substitution is also present at 7 K, but the spectral DOS within 30 meV of $E_F$ increases as shown in Fig. 8.5 on an enlarged energy scale. Although the substitution-induced change in the spectra extends up to $\sim -0.3$ eV, the position of the broad peak at $\sim -0.3$ eV does not show a substantial change.

Temperature-dependent spectral DOS of each sample is shown in Fig. 8.6, where the photoemission spectra have been divided by the FD function convoluted with a Gaussian corresponding to the instrumental resolution. The spectra have also been normalized below $-0.4$ eV. The temperature-dependent depression of the spectral DOS disappears in the $x = 0.30$ spectra.
8.3. Results and Discussion

Substitution dependence of the depression at various energies are plotted in Fig. 8.7. The depression in going from $x = 0.30$ to $x = 0.10$ is almost energy independent, indicating that the pseudogap is deepened uniformly. In going from $x = 0.10$ to 0.05 and 0.02, the depression within 50 meV of $E_F$ increases while that below $-100$ meV decreases. This means that the pseudogap of larger than $\sim 50$ meV opens between $x = 0.10$ and 0.05. Note that the negative slope in the $T$-$\rho$ curve appears at low temperatures for $x \sim < 0.10$ [8.8]. In going from $x = 0.02$ to 0.00 the curves show an energy-independent shift again\(^2\).

Based on the hybridization gap model for the Kondo insulators, hybridization between the conduction band and the localized band develops a gap sandwiched by a high DOS. Recent tunneling spectroscopy of FeSi [8.12] reveals the quasiparticle DOS peaks evolves at 50-70 mV on the both side of a gap on cooling. On the other hand, no growth

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\(^2\) This shift corresponds to a uniform depression of the DOS for $x = 0.00$ at 7 K, as is visible in Fig. 8.6 (a) and (b) while such a depression is absent in the raw spectra. Probably the background slope at 7 K was different from those at other temperatures for $x = 0.00$. 

Figure 8.5: Difference spectra at 7 K plotted on an enlarged energy scale.
corresponding to such quasiparticle DOS is observed in the photoemission spectra of FeSi on cooling and the DOS is monotonously decreased with lowering temperature\(^3\).

However, a broad peak develops around \(E_F\) with decreasing Al concentration as shown in Fig. 8.4 (a) and (b). Here we have subtracted the \(x = 0.30\) DOS at 7 K from the other DOS and have presented the temperature dependence of the difference DOS of each sample [Fig. 8.8 (a)] and the substitution dependence of the difference DOS at each temperature [Fig. 8.8 (b)]. Temperature dependence appears mainly from \(E_F\) to \(\sim -100\) meV in the \(x = 0.00, 0.02, 0.05,\) and 0.10 spectra. Especially, the depression of FeSi at low temperature in the vicinity of \(E_F\), which is recovered with a

\(^3\) Saitoh et al. [8.13] compared the photoemission spectra of FeSi with the DOS from the band-structure calculation [8.3] corrected with a model self-energy and pointed out that due to a strong band narrowing the peak of the quasiparticle DOS is located just \(\sim 10\) meV below \(E_F\) although the photoemission spectrum showed a maximum around \(\sim -0.3\) eV.
8.3. Results and Discussion

Figure 8.7: Substitution-dependent depression of the spectral DOS from 295 K to 7 K at various energies. The DOS values are from Fig. 8.6, where the spectra have been normalized below $-0.4$ eV.

small substitution as presented in Fig. 8.4 (a), is sensitive also to a small temperature increase. No temperature dependence appears in the $x = 0.30$ spectra as shown in the bottom panel of Fig. 8.8 (a). On the other hand, a strong substitution dependence remains down to $\sim -250$ meV or further below. As already mentioned for Fig. 8.4, the substitution dependence becomes strong with increasing temperature. Such strong substitution dependence at high temperatures is not present in the spectral DOS of Yb$_{1-x}$Lu$_x$B$_{12}$.

Note that in Fig. 8.8 the difference DOS at 150 K, 225 K, and 295 K grows in proportion to the deviation of Al content from $x = 0.30$. Such a smooth evolution of the DOS with substitution would also be present at lower temperatures but would be compensated with the pseudogap opening. In particular, the bottom panel of Fig. 8.8 (b) shows an apparent temperature independence of the spectral DOS below $\sim -50$ meV.

Tonogai et al. have measured the optical reflectivity of the same samples and deduced the optical conductivity [8.14] as shown in Fig. 8.9. The overall temperature
Figure 8.8: Difference DOS of FeSi$_{1-x}$Al$_x$ from the DOS of FeSi$_{0.70}$Al$_{0.03}$ at 7 K. (a) Temperature dependence for each composition, $T = 7$ K (thick curve), 75 K, 150 K, 225 K, and 295 K from bottom. (b) Substitution dependence at each temperature. The thick solid curves represent the DOS of the $x = 0$ sample, the dashed curves $x = 0.02$, the thick curves $x = 0.05$, the dot-dashed curves $x = 0.10$, and the solid dashed curves $x = 0.30$. 
Figure 8.9: Optical conductivity of FeSi$_{1-x}$Al$_x$ polycrystals [8.14].
dependence of the optical conductivity of FeSi does not depend on a slight Al substitution. The merging point of the temperature-dependent conductivity remains \( \sim 0.8 \) eV in the \( x = 0.02 \) and 0.05 samples while the conductivity within the gap grows with the substitution. On the other hand, the conductivity of the \( x = 0.10 \) sample is drastically different from the others: The temperature dependence mostly disappears and the shoulder of the gap edge, which is observed in the \( x = 0.00, 0.02, \) and 0.05 conductivity at \( \sim -0.1 \) eV, is smeared out. Both the PES spectra and the optical-conductivity spectra support that for \( x < \sim 0.05 \) the gap structure of FeSi survives whereas a new component evolves in the gap.

It should be noted that the effect of temperature and substitution on the spectral DOS of FeSi strongly depends on the energy although the line shape of the photoemission spectra of FeSi is rather simple, showing only one peak at \( \sim -0.3 \) eV. The spectral DOS in the vicinity of \( E_F \) (down to \(-20\) meV) is recovered with a slight substitution at 7 K and would most purely reflect the effect of a slight substitution. The temperature-dependent depression of the spectral DOS extends down to \( \sim -50 \) meV and the size of that pseudogap region is almost independent of \( x \). The shoulder at \( \sim -100 \) meV is reduced with Al substitution but shows no temperature dependence. The spectra in the energy region higher than the broad peak at \( \sim -300 \) meV does not depend on temperature nor substitution. The stability of the broad peak against substitution and temperature suggests that it does not influence the low-energy electronic properties of FeSi unlike the Kondo peak in \( f \)-electron systems.

In the photoemission spectra of YbB\(_{12}\), the Kondo peak appeared at the energy position of \( 3 \ k_B T_{\text{max}} \) as in a Kondo metal [8.15], where \( T_{\text{max}} \) is the temperature at which the susceptibility shows a maximum. For FeSi, \( T_{\text{max}} \) is \( \sim 500 \) K and hence \( 3 \ k_B T_{\text{max}} \) gives 0.13 eV. This corresponds to the shoulder in the photoemission spectrum of FeSi, not the broad peak at \( \sim -0.3 \) eV. Remember that the relation \( k_B T_K = 3 \ k_B T_{\text{max}} \) is given for a Ce-based Kondo metal [8.16]. Since the missing Pauli paramagnetism would have shifted \( T_{\text{max}} \) to higher temperature in FeSi, the magnetic susceptibility of FeSi would indicate that the upper limit of \( T_{\text{max}} \) is \( \sim 500 \) K. Thus the broad peak at \( \sim -0.3 \) eV can not be interpreted as the Kondo peak even if hypothetical “metallic FeSi” is considered. Sales et al. measured the magnetic susceptibility of FeSi and Fe\(_{0.90}\)Ir\(_{0.10}\)Si up to 800 K and found that the maximum of \( \sim 500 \) K in FeSi is slightly shifted to lower temperature by about \( \sim 100 \) K [8.17] with Ir substitution. The high-
temperature magnetic susceptibility$^d$ of FeSi$_{1-x}$Al$_x$ would be helpful to understand the photoemission spectra on the energy scale higher than the (pseudo)gap.

Finally, we compare the present result with that of Fe$_{1-x}$Co$_x$Si. In contrast with the spectral DOS of Fe$_{1-x}$Co$_x$Si, where the temperature-dependent depression on cooling from 295 K to 18 K survives almost fully in the $x = 0.10$ sample, the depression appears more sensitive to the Al substitution than the Co substitution although the electrical resistivity of Fe$_{1-x}$Co$_x$Si is almost the same as that of FeSi$_{1-x}$Al$_x$ [8.8]. Surviving pseudogap in Fe$_{1-x}$Co$_x$Si is remarkable because the Fe 3d states dominate the electronic structure around $E_F$ in FeSi and thus the Fe-site substitution may be expected to change the low-energy electronic states of FeSi to a larger extent than the Al-site substitution. The energy region where the pseudogap opens on cooling is $\sim 50$ meV from $E_F$, independent of a small substitution of both Al and Co. Under the present normalization, raising the temperature increases the spectral DOS in any energy position while a slight ($x \leq 0.05$) Al substitution at low temperature increases the spectral DOS at $E_F$ and simultaneously decreases the DOS between $-30$ meV and $-300$ meV.

### 8.4 Summary

We have studied the electronic states in FeSi$_{1-x}$Al$_x$ by temperature-dependent photoemission measurements. In spite of its structureless line shape, the response of the photoemission spectrum of FeSi to temperature or substitution is different in different energy regions. The dip in the vicinity of $E_F$ ($\sim -20$ meV) is filled for a small amount of Al substitution or a small temperature increase. The pseudogap region ($\sim -50$ meV) monotonously depends on the temperature and the Al substitution. The shoulder around $\sim -100$ meV, which is expected to correspond to the Kondo peak in a Kondo metal, depends on the Al substitution up to $x = 0.30$. The broad peak at $\sim -400$ meV is stable against both temperature and substitution.

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$^d$ Ohno et al. [8.8] and DiTusa et al. [8.11, 10] measured the magnetic susceptibility of FeSi$_{1-x}$Al$_x$ below room temperature.
References


Chapter 9

Conclusion

We have studied the electronic states in Kondo insulators YbB$_{12}$ and FeSi by high-resolution photoemission spectroscopy (PES). The principal results are schematically illustrated in Fig. 9.1 for YbB$_{12}$ and in Fig. 9.2 for FeSi. We have found that the observed position of the Kondo peak in YbB$_{12}$ agrees with the Kondo temperature ($T_K$) estimated from the magnetic susceptibility peak at $T \sim T_{\text{max}}$ (Fig. 9.1 (a)), indicating that single-site Kondo effect indeed governs the magnetic properties in this temperature range. By introducing a model self-energy to compare the photoemission spectra with first-principle band-structure calculation, the mass renormalization is shown to be strongly energy dependent near $E_F$. The density of states (DOS) of the B $2sp$ - Yb $5d$- derived conduction band is depressed near $E_F$. Lu substitution recovers the reduced conduction-band DOS, shifts the Yb $4f$-derived Kondo peak towards higher binding energy (Fig. 9.1 (a)) and decreases the Yb valence. These results are consistently analyzed using the Anderson impurity model. The temperature dependence of the B $sp$-derived conduction band of YbB$_{12}$ and Yb$_{1-x}$Lu$_x$B$_{12}$ has been measured with higher energy resolution. We have observed the temperature-dependent DOS which is consistent with its unusual magnetic susceptibility and electrical resistivity. A sharp dip of $\sim 10$ meV width appears at low temperatures ($< \sim 100$ K) in addition to the broad pseudogap of $\sim 100$ meV, which survives at room temperature (Fig. 9.1 (b)). Lu-substitution effect on YbB$_{12}$ is most clearly present at 7 K: In going from YbB$_{12}$ to LuB$_{12}$ the sharp (pseudo)gap at $E_F$ is filled and the broad peak at $\sim -80$ meV, which has been identified by comparison with the spectra of LuB$_{12}$, is reduced (Fig. 9.1 (b)). Such $x$ dependence disappears at higher temperatures, indicating a decoupling between the $f$ electrons and the conduction electrons above $\sim T_K$. The sharp depression at $E_F$
has shown a nonlinear response to $x$ and has appeared only for $x \leq 0.25$, presenting the effect beyond the single-site mechanism for the gap formation.

![Diagram](image)

Figure 9.1: Schematic summary of the photoemission spectra of YbB$_{12}$ and Yb$_{1-x}$Lu$_x$B$_{12}$: Kondo peaks in the $4f$ spectra (a) and the temperature dependence of the (pseudo)gap in the conduction-band spectra of YbB$_{12}$ and LuB$_{12}$ (b).

As for FeSi, we have studied the response of the electronic states to temperature and Fe-site or Si-site substitution. In spite of its structureless line shape, where only one peak appears at $\sim -0.4$ eV (Fig. 9.2 (a)), the response of the photoemission spectrum of FeSi to temperature and substitution is different at different energy regions. Though Co substitution for the Fe site changes not only the vicinity of $E_F$ but also the broad peak due to the difference in the $3d$ levels of Fe and Co, it affects mainly
low-temperature and low-energy electronic structure of FeSi and recovers the DOS in the vicinity of $E_F$, consistent with the optical conductivity and the dc conductivity. A systematic substitution effect on FeSi has been studied thoroughly in FeSi$_{1-x}$Al$_x$. The depression in the vicinity of the Fermi level ($\sim -20$ meV) is filled with a small amount of Al substitution (Fig. 9.2 (b)) and temperature increase. The pseudogap region ($\sim -50$ meV) depends on the temperature and the Al substitution (Fig. 9.2 (c)). The shoulder around $\sim -100$ meV, which may correspond to the Kondo peak in 4f-electron systems, depends on the Al substitution up to $x = 0.30$ (Fig. 9.2 (b)) and such substitution dependence of the shoulder is enhanced at higher temperature. The broad peak at $\sim -400$ meV is stable against both temperature and substitution.

A clear difference between YbB$_{12}$ and FeSi appears in the substitution dependence. The disappearance of the gap has been observed at $x \sim 0.25$-0.5 in Yb$_{1-x}$Lu$_x$B$_{12}$ and $x \sim 0.1$ in FeSi$_{1-x}$Al$_x$. These critical concentrations ($x_c$) are consistent with the transport properties. The rapid collapse of the gap with substitution indicates the importance of the intersite interaction for the gap opening in FeSi. While the gap in Yb$_{1-x}$Lu$_x$B$_{12}$, which survives up to $x \sim 0.25$-0.50, reflects the localized character of the 4f states, the $x$-nonlinearity of the substitution dependence of the photoemission spectra indicates an effect of the intersite interaction in the gap formation for YbB$_{12}$. The difference in $x_c$ might be one of the origin of the relatively high residual DOS for FeSi: At and around the scraped surface, where the atomic coordination is not perfect, the gap character would be more robust for YbB$_{12}$.

The relation between the peak position in the photoemission spectra and $T_{\text{max}}$, where the magnetic susceptibility shows a maximum, is different between YbB$_{12}$ and FeSi. The sharp Kondo peak, which is observed in the Yb Kondo systems, does not appear in FeSi. However, the substitution dependence of the spectra of FeSi at low temperatures resembles that of YbB$_{12}$ and is reminiscent of the hybridization gap model.
Figure 9.2: Schematic summary of the photoemission spectra of FeSi$_{1-x}$Al$_x$, which was studied in the wide $x$ range compared with Fe$_{1-x}$Co$_x$Si: The entire valence band which has a broad peak (a), the substitution dependence near $E_F$ (b), and the temperature dependence of the pseudogap around $E_F$ (c).
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